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APPLIED CHEMISTRY

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The Chemistry of Petroleum and its Substitutes. A Practical Handbook. By C. K. TINKLER, D.Sc. (Birm.), B.Sc. (Lond. and Wales), and F. CHALLENGER, Ph.D. (Gottingen), B.Sc. (Lond.), F.I.C., Lecturers in Chemistry in the University of Birmingham. With an Introduction by Sir BOVERTON REDWOOD. 368 pages. Medium 8vo .. .. *Net* **12s. 6d.**

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APPLIED CHEMISTRY

A PRACTICAL HANDBOOK FOR STUDENTS OF HOUSEHOLD SCIENCE AND PUBLIC HEALTH

BY

C. KENNETH TINKLER,

D.Sc., F.I.C.,

READER IN CHEMISTRY IN THE UNIVERSITY OF LONDON,
HEAD OF THE CHEMISTRY DEPARTMENT, KING'S COLLEGE FOR WOMEN
(HOUSEHOLD AND SOCIAL SCIENCE DEPARTMENT)

AND

HELEN MASTERS,

B.Sc. AND KING'S COLLEGE DIPLOMA IN HOUSEHOLD SCIENCE

LECTURER IN CHEMISTRY, KING'S COLLEGE FOR WOMEN (HOUSEHOLD AND
SOCIAL SCIENCE DEPARTMENT)

VOLUME I.

WATER, DETERGENTS, TEXTILES, FUELS, ETC.

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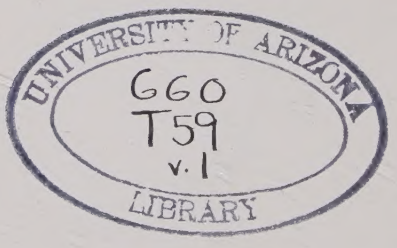

PREFACE

The University of London has recently instituted a Diploma in Household and Social Science, which is awarded to students who take a three years' course in the Household and Social Science Department of King's College for Women, and who pass the University examination in the various subjects of the course.

This University Diploma replaces that which has been given by the College for some years past.

In the first year of the course the standard of the work in Inorganic Chemistry is practically the same as that of an ordinary Intermediate B.Sc. course. In the second year a study is made of such Organic and Physical Chemistry as will serve as a basis for the courses of instruction in Applied Chemistry and Physiology. In addition, the students also gain further experience of quantitative methods.

In the course of Applied Chemistry, in the third year, it has been found impossible to make use of any one existing text-book for either the theoretical or practical work, and it is hoped that this book will supply a want which has been felt for some time, not only in this college, but also in other universities and training schools.

The lectures of the Applied Chemistry course deal

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more especially with the theoretical aspect of the subject, and although it is intended that this volume should be primarily a practical book, in some cases a certain amount of theoretical matter has been introduced.

The experiments described deal with Water Analysis, Detergents, Textile Fabrics, Bleaching Agents, Ventilation, Fuels, Paints, Polishes, etc. A second volume dealing with Foods is in preparation.

Some of the experiments described are of a very elementary character and in the ordinary way are not carried out by third year students, as they have previously been performed by them in connection with the courses in Physics and Pure Chemistry. On the other hand, some of the experiments described are only performed in the lectures.

In some cases the experiments deal more particularly with problems relating to household matters, and are not performed in the Chemical Laboratory, but form part of the work in the Kitchen Laboratory. This work is carried out in conjunction with the work in Applied Chemistry to meet the special needs of students of Household Science. Such experiments, denoted by two asterisks, are of a more specialised nature than the majority of those described.

Although the book is primarily intended for students in their third year, certain portions of it may be used for the instruction of other students who have not previously taken the two years' instruction in Pure Chemistry.

It is also hoped that the complete book will be of use to students preparing for the Diplomas and Degrees in Public Health of the various universities.

We wish to take this opportunity of expressing our thanks to Sir Herbert Jackson and Mr. H. L. Smith,

who initiated the course in Applied Chemistry, for the great assistance we have received from their work.

We also wish to thank Dr. J. J. Fox, of the Government Laboratory, for information with regard to the methods of analysis of paints, polishes, etc.

For the use of blocks for illustrations we are much indebted to Messrs. Baird & Tatlock (London) Ltd., Messrs. J. J. Griffin & Sons, Messrs. Alexander Wright & Co. Ltd., and the Richmond Gas Stove and Meter Co. Ltd.

C. K. T.
H. M.

King's College for Women,
Campden Hill Road,
Kensington, W.

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Chapter I.

WATER ANALYSIS.

In this course we are concerned only with the actual chemical operations involved in the determination of those constituents of natural waters which are taken into consideration in arriving at a decision as to whether or not a given water is fit for domestic purposes. The correct interpretation of these results, and also a study of the evidence as to the suitability of a water for a particular purpose, obtained from a bacteriological examination and from an inspection of the source of a water, is dealt with in another part of the course.

It should be pointed out that in most cases the substances to be determined are present in very minute quantities, and considerable skill and attention to detail are required in order to obtain results which shall be of any value.

The methods to be described include those which are usually employed for the determination of total solids, free and albuminoid ammonia, chloride, nitrates and nitrites, oxygen absorbed and hardness. The action of water on lead is also considered.

TAKING A SAMPLE OF WATER FOR ANALYSIS.

Allow at least 10 gallons of water to run to waste before collecting a sample for analysis, and make sure that the water is drawn from a tap attached directly to the water main and not from one to which the water is supplied from a cistern. It is extremely important that the bottle in which the water is collected should be perfectly clean, and it should not have been used previously for storing a solution of ammonia or an ammonium salt.

PRELIMINARY TESTS.

(*a*) Test with red and blue litmus paper to ascertain if the water is alkaline or acid to litmus.

(*b*) Warm some of the water in a test-tube and notice if there is any smell. A polluted water may evolve sulphuretted hydrogen.

FIG. 1.

(*c*) Allow some of the water to stand in a conical settling tube (Fig. 1). By turning the stopper of the tube through a right angle any sediment which has settled in the depression in the stopper may be separated from the large volume of water above it. Any sediment thus obtained should be examined under the microscope, see Plates in "The Examination of Waters and Water Supplies," by Thresh (Churchill).

TOTAL SOLIDS.

Clean thoroughly (inside and outside) a 3″ porcelain * (or platinum) basin. Dry in the steam oven for at least half an hour, cool in a desiccator and weigh accurately.

Place 50 c.c. of the water (measured with a pipette) in the basin and evaporate on a water bath; when nearly dry add another 50 c.c. of water and evaporate to dryness.

Clean the outside of the dish and heat in the steam oven for one hour.

Cool in a desiccator and when cold weigh quickly, as the residue will probably be deliquescent.

Reheat in steam oven for half an hour and continue the process until the weight is constant.

Express the result as Total Solids per 100,000 parts of water.

(Note *milligrams* per 100 c.c. = parts per 100,000.)

The amounts of the various constituents of natural waters are usually expressed as parts per 100,000; they are, however, sometimes represented as grains per gallon. Since 1 gallon of water = 70,000 grains, parts per 100,000 × 0·7 = parts per 70,000, i.e. grains per gallon.

The results obtained may vary from about 4 parts per 100,000 for an upland surface water to 60 or more parts per 100,000 for a shallow well water. A water containing more than 50 parts of total solids per 100,000 will usually be unsuitable for domestic purposes.

After the weighing of the dish for total solids is completed,

* A round-bottomed glass basin is more suitable if the residue is not to be ignited.

if a porcelain basin has been used, ignite the residue over a Bunsen burner and note that charring takes place, due to the presence of organic matter in the residue.

For the methods employed for the quantitative analysis of the residue obtained by the evaporation of a water, see "The Examination of Waters and Water Supplies," by Thresh (Churchill).

FREE (AND SALINE) AMMONIA.

In this process a measured volume of the water is distilled with a little sodium carbonate. The minute quantity of ammonia which is present in the water, either in the free state or as ammonium salts, as a result of the decomposition of nitrogenous organic matter, is obtained in the first portion of the distillate, and its amount is determined colorimetrically by means of Nessler solution. This solution contains mercuric iodide dissolved in water containing potassium iodide and potassium hydroxide.

The compound $HgI_2 . 2KI$ or K_2HgI_4 is soluble and colourless. By the action of ammonia on this substance a yellowish-brown insoluble substance, dimercuric-ammonium iodide, is produced as follows:—

$$2Hg''I_2 + 4NH_3 \rightarrow NHg''_2I + 3NH_4I.$$

This reaction affords an extremely delicate test for the presence of ammonia: even 1 part of ammonia in 100,000,000 of water can be detected by means of the reagent.

If the amount of ammonia is small no precipitate is obtained, but only a yellowish-brown coloration, and by matching the colour obtained on the addition of Nessler solution to a dilute solution of ammonia with that obtained by employing a solution of ammonium chloride of known concentration, the amount of ammonia present in the former solution is determined. The process is usually known as "nesslerising".

A solution of ammonium chloride is employed rather than a solution of ammonium hydroxide, as it would be impossible to keep such a dilute solution of ammonia at a definite concentration. The free alkali in the Nessler solution liberates the ammonia from the ammonium chloride.

The determination of ammonia in a water should, if possible, be carried out in a room in which no bottle containing ammonia solution is kept, and should be carried out as soon as possible after the bottle containing the sample has been opened.

Preparation of Solutions etc. required for the Determination of Free (and Saline) and Albuminoid Ammonia.

Nessler Solution.—Dissolve 62·5 gms. of potassium iodide in 250 c.c. of distilled water. To 240 c.c. of this solution add a saturated solution of mercuric chloride until a slight permanent precipitate persists after shaking. Add the remaining 10 c.c. of the potassium iodide solution, which will cause the precipitate to redissolve, and add gradually more of the saturated solution of mercuric chloride until a faint precipitate is produced.

Dissolve 150 gms. of potassium hydroxide in about 150 c.c. of distilled water and when cold mix with the potassium-mercuric iodide solution. Dilute to 1000 c.c., and after allowing the solution to stand decant the clear liquid into a bottle. The bottle should be fitted with a rubber bung and not with a glass stopper.

Ammonium Chloride Solution.—A solution of this salt is required containing ammonium chloride equivalent to 1 part of ammonia in 100,000 parts of water.

Owing to the very small amount of the salt which would be required to make up 1 litre of such a solution, it is usual to make in the first place a solution which is fifty times as concentrated as that finally required, i.e. 50 parts NH_3 per 100,000 c.c. or 0·25 part NH_3 per 500 c.c.

From the relation

NH_4Cl		NH_3
53·5 gms. NH_4Cl	contain	17 gms. NH_3
0·787 gm. ,,	contains	0·25 gm. ,,

Weigh out exactly 0·787 gm. of pure ammonium chloride, dissolve in ammonia-free water * and dilute to 500 c.c. Shake the solution well and dilute 10 c.c. of it to 500 c.c. with ammonia-free water.

1 c.c. of this solution = 0·00001 gm. NH_3, i.e. 1 part NH_3 per 100,000.

If 500 c.c. of the water under examination gave ammonia corresponding to 1 c.c. of this solution, it is obvious that

* If on testing the ordinary distilled water (50 c.c.) with 1 c.c. of Nessler solution in a cylinder more than the faintest coloration is observed after stirring and allowing to stand two minutes, the water should be re-distilled after the addition of a little sodium carbonate (see p. 3), the first portion of the distillate being rejected, and a stock of "ammonia-free" water obtained.

500 c.c. of the water contained 0·00001 gm. of free (and saline) ammonia.

$$\therefore \text{ 100,000 of the water contained } \frac{0{\cdot}00001 \times 100{,}000}{500} = 0{\cdot}002$$

gm. of free (and saline) ammonia.

That is, if 500 c.c. of water are employed for the test, each c.c. of the ammonium chloride solution required corresponds to 0·002 part of free (and saline) ammonia per 100,000.

Ignited Sodium Carbonate.—Heat a little pure sodium carbonate for half an hour in a procelain basin to drive off any ammonium salt which may be present as impurity. Sodium carbonate made by the ammonia-soda process invariably contains traces of ammonium salts, so that the ignition of this substance before use is essential.

Alkaline Permanganate (for albuminoid ammonia).—Weigh out approximately 50 gms. of potassium hydroxide. Dissolve in about 300 c.c. of water. Add 2 gms. of potassium permanganate and boil in a conical flask for about an hour.

Cool the solution and dilute to 250 c.c. For the experiment described on p. 8, 50 c.c. of this solution is diluted with distilled water to 250 c.c. and the mixture boiled for half an hour.

The Determination of Free (and Saline) Ammonia.

Fit up the apparatus as shown in the diagram (Fig. 2). The rubber bungs used should be such as are only employed for this particular determination.* Place about 700 c.c. of distilled water in the flask and add about 1 gm. of recently ignited sodium carbonate. Heat the flask over a wire gauze by means of a large burner and collect the distillate in a 50 c.c. Nessler cylinder. The distillate should be quite cold. To the second portion of the distillate (50 c.c.) add 1 c.c. Nessler solution by means of a graduated pipette. Stir with a glass rod and allow to stand for two minutes.

If any coloration is observed, when viewed from above over a white tile, distil further portions until one is obtained which gives no coloration with the Nessler reagent. When this is the case the apparatus is ammonia-free.

The apparatus is now ready to receive the water under

* A more suitable flask is one fitted with a ground-in glass stopper, as ammonia may be given off from the rubber bung and so render it difficult to obtain the apparatus "ammonia-free".

examination, but for practice in matching the colours of solutions it will be advisable to carry out a test in which the total amount of ammonia to be determined is known.

Cool the distilling flask under the tap and add 5 c.c. of the dilute solution of ammonium chloride * from a burette. [Take care that none of the solution runs down the side tube of the distilling flask.] If the volume of water in the flask is less than about half a litre add ammonia-free water to make it approximately this volume.

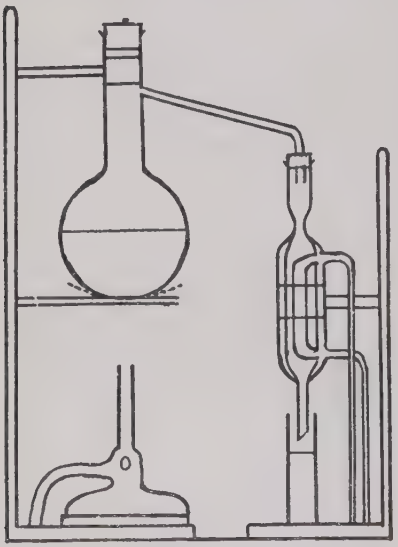


Fig. 2.

Add about 1 gm. of recently ignited sodium carbonate, distil and collect the distillate in 50 c.c. portions in four Nessler cylinders. The cylinders should be plainly marked in the order in which they are used.

To the contents of the *second* cylinder add 1 c.c. of Nessler solution, stir and allow to stand as before.

In a fifth cylinder place 1 c.c. of the dilute solution of ammonium chloride (1 c.c. = 0·00001 gm. NH_3) measured from a burette and add ammonia-free water to the 50 c.c. mark. Nesslerise as before and compare the colour obtained with that obtained in the second cylinder. If the colour observed in the comparison cylinder (No. 5) is too deep repeat the process, using 0·5 c.c. of the ammonium chloride solution. Similarly, if the colour observed in the comparison cylinder is too light repeat the process, using 1·5 or 2 c.c. of the ammonium chloride solution. Find out exactly how much of the ammonium chloride solution is required to match the colour. It should be noted that ammonium chloride solution should *not* be added to the cylinder *after* the Nessler solution has been added, or the solution becomes turbid.

After the colour in the second cylinder has been matched

* 1 c.c. = 0·00001 gm. NH_3, see p. 4.

the contents of the first, third, and fourth cylinders should be nesslerised, and the amounts of ammonia present determined as in the former case. The total volume of ammonium chloride solution required should obviously be 5 c.c., as this was the amount put into the flask. The reason for matching the colour of the *second* cylinder first is that if the second cylinder requires more than 5 c.c. of the ammonium chloride for matching, the first cylinder will contain so much ammonia that it cannot be nesslerised directly, on account of the depth of the colour which would be obtained. In such a case the contents of the first cylinder would be diluted to 250 c.c. and 50 c.c. of this diluted solution then nesslerised. In the present experiment, however, the second cylinder must obviously require considerably less than 5 c.c. of the ammonium chloride solution.

For the determination of the free (and saline) ammonia in the water under examination, when the apparatus is ammonia-free, place 500 c.c. of the water in the distilling flask, add about 1 gm. of recently ignited sodium carbonate and distil.* Collect the distillate, which should be quite cold, 50 c.c. at a time, in Nessler cylinders and continue the distillation until a portion of the distillate (50 c.c.) requires less than 0·25 c.c. of the ammonium chloride solution for matching the colour.

Nesslerise as before, using the second cylinder before the first for the reason given on page above.

[*Note.*—The water remaining in the flask will be required for the determination of the albuminoid ammonia.]

From the total volume of ammonium chloride solution required the amount of free (and saline) ammonia in 100,000 parts of the water may be calculated.

Example :—

2nd cylinder → 0·25 c.c. NH_4Cl
1st „ → 2·0 „ „
Total 2·25 „ „

∴ 500 c.c. of water contain 0·00001 × 2·25 gms. NH_3.

∴ 100,000 of water contain $0{\cdot}0000225 \times \frac{100{,}000}{500}$ gms. NH_3

= 0·0045 gm. NH_3.

* While the determination of the free ammonia is in progress, dilute 50 c.c. of the alkaline potassium permanganate solution (p. 5) to 250 c.c., and boil the solution for half an hour to remove any trace of ammonia. This solution is required in connection with the determination of the albuminoid ammonia (p. 8).

The amounts of free (and saline) ammonia in natural waters vary greatly. As a rule, considerably less than 0·01 part per 100,000 is found. It will be readily understood that the importance of the presence of such a minute amount of ammonia (or ammonium salts) in a water must be an indirect one. It will, however, be pointed out elsewhere that even such a small amount of free ammonia as 0·01 part per 100,000 would probably point to recent sewage contamination of the water, although it must be emphasised that no definite conclusion as to the purity of a water can be arrived at by the determination of any one constituent alone.

ALBUMINOID AMMONIA.

When all the free (and saline) ammonia has been removed the water remaining in the flask is distilled with a solution of alkaline potassium permanganate. The ammonia which is thereby produced results from the action of the alkaline permanganate on nitrogenous organic substances, such as uric acid etc., which do not give ammonia when boiled with a dilute solution of sodium carbonate. The amount of ammonia so obtained, known as the albuminoid ammonia, can be determined as in the case of the free ammonia.

The Determination of Albuminoid Ammonia.

The diluted solution of alkaline permanganate (50 c.c. of the original solution diluted to 250 c.c., see p. 5), which has been boiled for half an hour, is added to the water remaining in the flask after the determination of the free ammonia and the solution distilled. Care should be taken that none of the permanganate solution flows into the side tube of the flask.

Collect four portions of 50 c.c. in Nessler cylinders. Nesslerise the fourth first, and, if not free from ammonia, collect a fifth portion of the distillate. Nesslerise the third, second, and first cylinders, and from the total volume of ammonium chloride required for matching, calculate the amount of albuminoid ammonia per 100,000 of water.

It may be observed that the albuminoid ammonia is not evolved as rapidly as the free ammonia, and that the second cylinder often contains nearly as much ammonia as the first. This is due to the fact that many nitrogenous organic substances are decomposed only slowly by alkaline permanganate.

The amount of albuminoid ammonia in a drinking water does not as a rule exceed 0·008 part per 100,000, although considerable variations in the amount of this constituent are met with in different waters.

After the determination of the albuminoid ammonia the distillation flask should be cleaned by means of a small quantity of concentrated hydrochloric acid. The apparatus is required later for the determination of nitrate (see p. 11).

CHLORINE PRESENT AS CHLORIDE.

Chlorine is almost invariably in combination when present in water, usually in the form of sodium or calcium chloride.

The determination of the amount of chlorine as chloride is very easily carried out, and is of great importance in affording evidence as to whether or not a water is contaminated with sewage, which contains a very large amount of chloride. Unlike the nitrogenous constituents of water, chloride when once present in water cannot be removed by any natural process.

The possibility of the presence of chloride in a water due to admixture with mineral spring water or sea spray must not, of course, be overlooked.

The determination of the chloride in water is carried out by titration with a standard solution of silver nitrate, potassium chromate being used as indicator, as in the ordinary process for the determination of sodium chloride in solution. No red silver chromate is formed until all the chloride has been precipitated.

Solution of Silver Nitrate for Determination of Chlorine as Chloride in Water.—A solution of silver nitrate is required of which 1 c.c. = 0·0005 gm. Cl.

From the equation

$$\underset{170}{AgNO_3} + \underset{35{\cdot}5}{NaCl} \rightarrow NaNO_3 + AgCl$$

$$0{\cdot}0005 \text{ gm. Cl} = \frac{170}{35{\cdot}5} \times 0{\cdot}0005 \text{ gm. } AgNO_3.$$

$\therefore$ for 250 c.c. $AgNO_3$ solution the amount of $AgNO_3$ required $= \dfrac{250 \times 170 \times 0{\cdot}0005}{35{\cdot}5} = 0{\cdot}599.$

Weigh out on a watch glass 0·599 gm. silver nitrate, dissolve in distilled water and dilute to 250 c.c.

The Determination of Chlorine as Chloride.

Measure out, by means of a pipette, two portions of 50 c.c. of the water to be tested into two porcelain basins and add 2 drops of 10 per cent. potassium chromate solution to each. Run the silver nitrate solution from a burette 0·1 c.c. at a time into one portion and stir with a glass rod.

Continue the addition of the silver nitrate until a very faint red colour is perceptible, when the colour is compared with that of the second portion of the water. Repeat the experiment twice and take the average of the three readings.

It will be seen that if 50 c.c. of the water require 1 c.c. of the silver nitrate solution, of which 1 c.c. = 0·0005 gm. Cl, then 50 c.c. of water contain 0·0005 gm. Cl as chloride.

$$\therefore \text{ 100,000 of water contain } \frac{0{\cdot}0005 \times 100{,}000}{50} = 1{\cdot}0 \text{ parts}$$

of chlorine.

So that the number of cubic centimetres of the silver nitrate solution used for 50 c.c. of the water gives at once the parts of chlorine per 100,000 of the water.

As a rule the amount of chlorine as chloride per 100,000 present in a drinking water does not exceed 2 parts.

NITROGEN AS NITRATE AND NITRITE.

The ammonia which occurs in natural water, as a result of the decomposition of nitrogenous organic matter, is oxidised first to nitrite and then rapidly to nitrate. Some of the nitrate may, however, be again reduced to nitrite by means of a second contact with organic matter or a ferrous compound.

Nitrate is invariably a constituent of a drinking water, whereas nitrite is very rarely present.

Various methods are employed for the determination of nitrogen as nitrate and nitrite.

In Crum's method the residue obtained in the determination of total solids is treated with concentrated sulphuric acid in presence of mercury. The apparatus employed consists of a special form of Lunge nitrometer in which the nitric oxide evolved is measured. From the volume of nitric oxide obtained the amount of nitrogen as nitrate and nitrite is found.

In another method the nitric acid obtained from the *nitrate*, by treatment with sulphuric acid, is allowed to act on phenol sulphonic acid, $C_6H_4(OH)SO_3H$, which is thereby converted

into picric acid, the sulpho group being eliminated during the nitration :—

$$C_6H_4(OH)(SO_3H) + 3(HO \cdot NO_2) \rightarrow C_6H_2(NO_2)_3OH + H_2SO_4 + 2H_2O.$$

The amount of picric acid produced is determined colorimetrically after conversion into ammonium picrate, which is a substance having an intense yellow colour. In this method the nitrate only is determined.

In a third method the nitrate and nitrite are reduced by means of nascent hydrogen (zinc-copper couple) to ammonia, which can then be determined in the ordinary way by distillation and nesslerising. This method is described in detail below. A method employed for the determination of nitrite alone is described on p. 13.

Determination of Nitrate and Nitrite by Reduction to Ammonia. (Zinc-Copper Couple Method.)

Place about twenty strips of zinc foil (about 4 ins. × ½ in.) in a 200 c.c. reagent bottle. Clean the zinc by treatment with water containing a little dilute sulphuric acid, then wash well with distilled water. Fill the bottle with a 1 per cent. solution of copper sulphate and allow the zinc to remain in contact with this solution for fifteen minutes. Pour out the solution of copper sulphate and wash five or six times with distilled water. The zinc should now be coated with a black adherent film of copper. $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$.

Fill the bottle with the water under examination, add about 0·1 gm. of oxalic acid, stopper loosely and allow to stand overnight.

The oxalic acid is added to accelerate the reaction. The nitrate and nitrite are reduced to ammonia by the nascent hydrogen as follows :—

$$NaNO_3 + 8H \rightarrow NaOH + 2H_2O + NH_3.$$

Owing to the presence of oxalic acid, however, sodium and ammonium oxalates are produced and not free sodium hydroxide and ammonia.

If the reduction to ammonia is complete, no coloration should be obtained on testing for nitrite by means of m.phenylene-diamine and sulphuric acid (see p. 13), or by means of a solution of sulphanilic acid, phenol and ammonia (see p. 13).

The next operation consists in determining the amount of

ammonia produced. Place 700 c.c. of distilled water in the distilling flask of the ammonia apparatus (Fig. 2), add a little freshly ignited sodium carbonate and distil until the apparatus is ammonia-free.

When this is the case, cool the distilling flask under the tap and add 50 c.c. of the water which has been treated with the zinc-copper couple and more ammonia-free water if necessary.

Proceed as in an ordinary determination of free ammonia. In this case it is very important to nesslerise the second cylinder first, as the amount of ammonia may be considerable. From the amount of the standard solution of ammonium chloride required, calculate the amount of ammonia present in 50 c.c. of the water which has been treated with the zinc-copper couple. Since $\frac{14}{17}$ of this ammonia is nitrogen, the amount of nitrogen as nitrate and nitrite in 100,000 parts of water is readily found.

If the water contained free ammonia before treatment with the zinc-copper couple a deduction must be made for the amount of free ammonia in 50 c.c.

Example :—

2nd cylinder required		5·5 c.c. NH_4Cl
3rd „ „		2·0 „ „
4th „ „		0·5 „ „
5th „ free		
1st cylinder after dilution to 250 c.c.		
50 required 3·5 c.c. NH_4Cl	∴ 250 =	17·5 „ „
	Total	25·5 „ „

But 500 c.c. of the original water contained free ammonia equivalent to 2·25 c.c. of the standard solution of ammonium chloride.

∴ 50 c.c. contained free ammonium equivalent to 0·225 c.c. NH_4Cl solution.

∴ The ammonia from nitrate and nitrite in 50 c.c. of the water is equivalent to 25·5 − 0·225 = 25·3 c.c. NH_4Cl

1 c.c. NH_4Cl solution = 0·00001 gm. NH_3.

∴ 25·3 „ = 0·000253 „ „

$\frac{14}{17}$ of 0·000253 = 0·00021 gm. nitrogen.

∴ 50 c.c. of original water contained 0·00021 gm. nitrogen as nitrate and nitrite.

∴ 100,000 of original water contained 0·00021 × 2000 = 0·42 gm. nitrogen as nitrate and nitrite.

This water was found to contain no nitrite before reduction, so that nitrogen as nitrate = 0·42 part per 100,000.

The amount of nitrogen as nitrate present in a water varies very considerably according to the source of the water. An upland surface water may contain as little as 0·01 part per 100,000, whereas in a deep well water it is quite usual to find as much as 0·6 part per 100,000.

NITROGEN AS NITRITE.

For the detection of nitrite in water use is made of the well-known formation of a diazo compound by the interaction of a primary aromatic amino compound and nitrous acid, with the subsequent "coupling" of the diazo compound with a phenol or primary amine, which gives rise to an azo dye.

By comparing the colour produced on treatment of the water with that produced from a solution of a nitrite of known concentration the amount of nitrite present in the water may be determined.

The aromatic amino compound employed in one method is m.phenylene-diamine, $C_6H_4(NH_2)_2$. A solution of this substance in dilute sulphuric acid, on treatment with nitrous acid, gives the semi-diazo compound $NH_2C_6H_4 . N : N . HSO_4$, which couples with another molecule of the phenylene-diamine to form the brown azo dye,

$$(NH_2)C_6H_4N : NC_6H_3(NH_2)_2.$$

If on treating a sample of water (about 50 c.c.) with about 2 c.c. of dilute sulphuric acid and 1 c.c. of a 0·5 per cent. solution of m.phenylene-diamine in dilute sulphuric acid, a brown coloration is produced, the presence of nitrite in the water is inferred.

In another method the amino compound employed is sulphanilic acid, $C_6H_4(SO_3H)NH_2$. This after diazotisation is treated with an aqueous solution of phenol and the whole rendered alkaline with ammonia. A yellow dye is thus produced. The reactions may be represented as follows:—

$$C_6H_4(SO_3H)N\boxed{H_2 + O}N . OH \rightarrow C_6H_4(SO_3H)N : NOH$$

sulphanilic acid nitrous acid

$$C_6H_4(SO_3H)N : N\boxed{OH + H}C_6H_4OH$$

phenol

$$\rightarrow C_6H_4(SO_3H)N : NC_6H_4OH$$

azo compound

The ammonium derivative produced by the action of ammonium hydroxide is the actual dye.

Solutions Required. — A solution of *sodium nitrite* is required containing 1 part of nitrous anhydride (N_2O_3) in 100,000 of water.

For accurate work this solution is usually made from silver nitrite by double decomposition with sodium chloride, as silver nitrite is more easily obtained in a pure state than sodium nitrite.

For the present purpose it may be assumed that crystallised sodium nitrite is pure, and the solution made directly from this substance. From the relation between N_2O_3 and $2NaNO_2$ (or $Na_2O \cdot N_2O_3$) it will be seen that 76 gms. of N_2O_3 are contained in 138 gms. of $NaNO_2$, or 1 gm. N_2O_3 is contained in 1·9 gms. $NaNO_2$.

Hence 1·9 gms. of sodium nitrite in 100,000 c.c. of water would give a solution containing 1 part of N_2O_3 per 100,000 of water.

1·9 gm. per 100,000 = 0·19 per 10 litres,
or 0·019 per litre.

Weigh out on a watch glass exactly 0·19 gm. pure $NaNO_2$, dissolve in water and dilute to 1 litre. This solution is ten times the concentration of that required. Shake the solution well, measure out 25 c.c. with a pipette and dilute to 250 c.c. 1 c.c. of this solution = 0·00001 gm. N_2O_3, or the solution contains 1 part N_2O_3 per 100,000 of water.

Saturated solutions of *sulphanilic acid* in dilute sulphuric acid and of *phenol* in water are also required.

The Determination of Nitrite.

In six Nessler cylinders place 0·4, 0·8, 1·0, 1·2, 1·6, and 2·0 c.c. of the dilute sodium nitrite solution. Dilute to 50 c.c. in each case with distilled water. In another cylinder place 50 c.c. of the water under examination.

To each cylinder add $\frac{1}{2}$ c.c. of the sulphanilic acid solution. Allow to stand for ten minutes, add $\frac{1}{2}$ c.c. of the phenol solution and make alkaline with ammonia.

Compare the colour of the solution in the test cylinder with that of the other solutions and in this way determine the amount of nitrogen as nitrite in the sample of water.

If 50 c.c. of the water under examination gave a colour which is matched by 1·0 c.c. of the standard nitrite solution,

since 1 c.c. of the standard nitrite solution = 0·00001 gm. N_2O_3, the amount of N_2O_3 per 100,000

$$= 1 \times 0{\cdot}00001 \times \frac{100{,}000}{50}$$
$$= 0{\cdot}02.$$

Although it is claimed that 1 part of N_2O_3 in 40 million of water can be detected by this test it is unlikely that the water under examination will give a positive reaction for nitrite. For practice in the determination, however, a measured volume of the standard nitrite solution should be added to 1 litre of distilled water and the amount of nitrite in solution then determined.

For the detection of nitrite in flour after bleaching with nitrogen peroxide see Vol. II.

In connection with the presence of nitrite in water it should be noted that it has recently been shown by B. Moore (Proc. Roy. Soc. 1918 [B], **90**, 158) that dilute solutions of nitrates exposed to sunlight, or other light rich in ultra-violet rays, give the reaction characteristic of nitrites.

OXIDISABLE ORGANIC MATTER IN WATER. "OXYGEN ABSORBED."

In the process usually adopted for the determination of the amount of organic matter in water, a measured volume of the water is treated with excess of a standard solution of potassium permanganate in presence of sulphuric acid. The experiment is carried out under certain standard conditions, and although the method does not afford a measure of the absolute amount of organic matter present, from the amount of potassium permanganate decomposed by the water it is possible to obtain evidence as to the relative amounts of organic matter in different waters.

Other principles involved in the process are (*a*) the liberation of iodine from a solution of potassium iodide by the action of potassium permanganate in presence of sulphuric acid, and (*b*) the determination of the amount of iodine liberated by titration with a solution of sodium thiosulphate. From the difference in the amount of the thiosulphate solution required for a given volume of the potassium permanganate before and after treatment with the water the amount of potassium permanganate decomposed, and hence the amount of oxygen absorbed by the water, is determined.

The reactions may be represented as follows :—

$K_2Mn_2O_8$ or 316 gms.

$$\begin{cases} K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O \\ 2MnO + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O \\ 5O \text{ (oxygen available for oxidation) } 80 \text{ gms.} \end{cases}$$

$$a. \begin{cases} K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O \\ 2MnO + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O \\ 5O + 10HI \rightarrow 5H_2O + 5I_2 \end{cases}$$

$$b.\ 2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Solutions Required :—

1. A solution of *potassium permanganate* containing 0·1 gm. available oxygen per litre, i.e. 1 c.c. = 0·0001 gm. available oxygen. It will be seen from the equations given above that 316 gms. of potassium permanganate in presence of sulphuric acid afford 80 gms. of available oxygen. Hence 0·1 gm. available oxygen is contained in $\frac{316}{80} \times 0{\cdot}1$ gm. = 0·395 gm. of potassium permanganate.

Weigh out exactly 0·395 gm. of finely powdered, pure potassium permanganate, treat with distilled water in a beaker, pour off the solution into a litre flask and repeat the process until the whole of the permanganate is dissolved. Dilute to 1 litre and shake the solution thoroughly.

2. A solution of *sodium thiosulphate* containing 1 gm. (approximately) of $Na_2S_2O_3 . 5H_2O$ in 1 litre of water.

3. A 10 per cent. solution of *potassium iodide.*

4. A solution of *starch*, which should be freshly made by grinding about 1 gm. of starch into a paste with cold water and then pouring into about 150 c.c. of boiling water.

5. Dilute *sulphuric acid*, 1 volume of concentrated acid to 3 volumes of water.

Determination of Oxygen Absorbed.

In each of two 500 c.c. glass-stoppered bottles put 250 c.c. of the water under examination, and in a third 500 c.c. bottle put 250 c.c. of distilled water. Label the bottles. To the contents of each add 10 c.c. of the dilute sulphuric acid and 10 c.c. of the potassium permanganate solution measured with a pipette. Place the three bottles in an oven at 80° F. (27° C.) and allow them to remain for four hours.

Four hours at 80° F. is usually the standard adopted for the test, but other standards, such as four hours at 98° F., three hours at 80° F. etc., are often employed.

For a rapid test five minutes at 80° F. is often employed, and for further practice in the determination it is advisable to carry out a test under these conditions.

Treat 250 c.c. of the water under examination and 250 c.c. of distilled water with 10 c.c. of dilute sulphuric acid and 10 c.c. of the potassium permanganate solution, and allow to remain in the air oven at 80° F. for five minutes.

Remove the two bottles from the oven, and to each add 5 drops of the 10 per cent. solution of potassium iodide.

Run the sodium thiosulphate solution from a burette into the bottle, which originally contained the distilled water, until only a faint yellow colour remains. Add starch solution and continue the addition of the sodium thiosulphate solution cautiously until the blue colour disappears.

Note the volume of sodium thiosulphate solution required for this blank experiment and repeat the process with the water under examination.

The calculation of the oxygen absorbed is made as in the following example :—

Blank Experiment.—250 c.c. *distilled water* + 10 c.c. dilute sulphuric acid + 10 c.c. $K_2Mn_2O_8$ solution (1 c.c. = 0·0001 gm. available oxygen).

After treatment in an air oven (five minutes at 80° F.) 5 drops of a 10 per cent. solution of potassium iodide added.

Volume of $Na_2S_2O_3$ solution required = 31·5 c.c.

∴ 31·5 c.c. of the $Na_2S_2O_3$ solution corresponds to 10 × 0·0001 gm. available oxygen,

$$\text{or 1 c.c. } Na_2S_2O_3 \text{ solution} = \frac{10 \times 0{\cdot}0001}{31{\cdot}5} = 0{\cdot}0000317 \text{ gm.}$$

available oxygen.

Test Experiment.—250 c.c. of water treated as above.

Volume of $Na_2S_2O_3$ solution required = 29·4 c.c.

Difference in reading between test and blank experiments, 31·5 − 29·4 = 2·1 c.c. $Na_2S_2O_3$ solution.

But 1 c.c. $Na_2S_2O_3$ solution corresponds to 0·0000317 gm. available oxygen.

∴ 2·1 c.c. corresponds to 2·1 × 0·0000317 gm. available oxygen = 0·00006657 gm. available oxygen.

This oxygen is absorbed by 250 c.c. of water.

∴ oxygen absorbed per 100,000 of water (5 minutes at 80° F.)

$$= \frac{0{\cdot}00006657 \times 100{,}000}{250} = 0{\cdot}0266.$$

At the expiration of four hours, remove the three bottles from the air oven and proceed exactly as described above. Carry out the blank experiment first and take the mean of the two results with the water under examination for the calculation of the oxygen absorbed.

It will be noted that the oxygen absorbed during four hours is considerably greater than that absorbed during five minutes. The results obtained for different waters vary considerably. For an upland surface water as much as 0·2 part of oxygen absorbed per 100,000 is quite a usual amount, whereas for a deep well water considerably less than 0·05 part per 100,000 may be found.

THE HARDNESS OF WATER.

The hardness, or soap-destroying power, of water is due to the presence in the water of calcium or magnesium carbonates, kept in solution in the form of soluble bicarbonates by means of the carbonic acid present in the water, or to the presence of substances such as calcium or magnesium sulphates.

The action of both calcium bicarbonate and calcium sulphate on a soap is of the same nature and leads to the formation of the insoluble calcium (or magnesium) salt of the acid contained in the soap.

Thus

$$\underset{\substack{100\\ \text{calcium bicarbonate (soluble)}}}{CaCO_3 . H_2CO_3} + \underset{\substack{612\\ \text{sodium stearate (soluble)}}}{2C_{17}H_{35}COONa} \rightarrow 2NaHCO_3 + \underset{\substack{\text{calcium stearate}\\ \text{(insoluble)}}}{Ca(OOC . C_{17}H_{35})_2}$$

$$CaSO_4 + \underset{\text{sodium oleate}}{2C_{17}H_{33}COONa} \rightarrow Na_2SO_4 + \underset{\substack{\text{calcium oleate}\\ \text{(insoluble)}}}{Ca(OOCC_{17}H_{33})_2}.$$

It will be obvious that so long as such calcium (or magnesium) salts are present in solution in the water no lather, due to solution of the unchanged soap, will be possible.

Hardness due to the presence of calcium and magnesium bicarbonates is known as *temporary* hardness and can be re-

moved simply by boiling, as these bicarbonates are decomposed on heating.

$$CaCO_3 . H_2CO_3 \rightarrow \underset{\text{ppt.}}{CaCO_3} + H_2O + CO_2$$

It may also be removed by the addition of lime

$$CaCO_3 . H_2CO_3 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O.$$

(See p. 46.)

Hardness due to the presence of calcium and magnesium sulphates is unaffected by boiling and is known as *permanent* hardness. Such hardness may be removed by the addition of sodium carbonate—

$$CaSO_4 + Na_2CO_3 \rightarrow \underset{\text{ppt.}}{CaCO_3} + Na_2SO_4.$$

(See also p. 47.)

From the equations given on p. 18, it will be seen that 100 gms. of calcium carbonate will precipitate 612 gms. of sodium stearate, corresponding to about 1000 gms. of an ordinary soap.* That is, every part of calcium carbonate in solution in water requires about 10 parts of soap for its removal. It will thus be obvious that it is often advantageous to employ some substance which is cheaper than soap to effect the removal of the calcium carbonate etc. from a water. (See Methods of Softening of Water, p. 48.)

One of the methods employed for the determination of the hardness of water is to find out how much of a standard solution of soap is required to produce a permanent lather with a definite volume of the water.

Unfortunately, the numerical expression of the hardness of water is represented in several different ways. In laundry practice in this country a water having 1° of hardness is usually understood to contain 1 grain of calcium carbonate, or its equivalent, in 1 gallon of water, i.e. 1 grain in 70,000 grains of water.

In more scientific work 1° of hardness is taken to correspond to 1 part of calcium carbonate, or its equivalent, in 100,000 parts of water.

A water having 10° of hardness is defined as one having ten times the soap-destroying power of one having 1° of hardness, but it is found in practice that a water containing, for example, 10 parts of calcium carbonate per 100,000 has considerably

* Owing to water content etc. of the soap (see p. 59).

less than 10 times the soap-destroying power of one containing 1 part of calcium carbonate per 100,000. That is, the soap-destroying power of a water is not directly proportional to the amount of calcium carbonate etc. contained in the water.

If, therefore, it is desired to express the hardness of a water in parts of calcium carbonate per 100,000, as is often the case, use is made of a table, which has been drawn up as the result of experiments, which shows the relation between the volume of a particular standard solution of soap required for a given volume of water and the parts per 100,000 of calcium carbonate contained in that water. For details of this method see Clowes and Coleman, "Quantitative Analysis" (Churchill).

THE DETERMINATION OF THE HARDNESS OF WATER BY MEANS OF A STANDARD SOAP SOLUTION.

The method to be described is that generally employed in connection with laundry work in this country; the hardness being expressed in degrees, on the basis 1° of hardness corresponding to 1 grain of calcium carbonate per gallon of water.

Solutions Required.

1. *Soap Solution.*—This solution is prepared by dissolving 10 gms. of Castile soap, cut in thin shavings, in a mixture of 500 c.c. of Industrial methylated spirit and 500 c.c. of water.

[*Note.*—Methylated spirit which has been denatured by the addition of paraffin must not be used for this purpose, as a turbidity is produced, due to the separation of the paraffin, on addition of water. Industrial spirit is denatured by the addition of crude wood spirit and does not become turbid on mixing with water.]

2. *Calcium Chloride Solution.*—Weigh out exactly 1 gm. of pure calcium carbonate. Powdered Iceland spar is the most suitable form of calcium carbonate for this purpose.

Transfer completely to a small porcelain dish by means of a *small* quantity of water and dissolve the calcium carbonate by the addition of the least possible quantity of dilute hydrochloric acid. Cover the dish with a clock glass to prevent loss until the effervescence has ceased. Wash the clock glass with distilled water and allow the washings to fall into the dish.

Evaporate the solution to dryness on the water bath, protecting the dish from dust by means of an evaporating funnel. Add a small quantity of water and again evaporate to dryness. This is to ensure the complete removal of the hydrochloric acid.

Add water to the contents of the dish and transfer to a litre flask. Wash out the dish into the flask and dilute the solution to 1 litre. Mix the solution thoroughly by shaking.

1 c.c. of this solution contains calcium chloride equivalent to 0·001 gm. of calcium carbonate.

Standardisation of the Soap Solution.

[Before proceeding with this experiment commence heating the water for the determination of permanent hardness, p. 23.]

Measure out 10 c.c. of the solution of calcium chloride with a pipette into a 200 c.c. glass-stoppered bottle. Add 60 c.c. of distilled water.

In the 70 c.c. of solution there is an amount of calcium chloride equivalent to 0·01 gm. or 10 mg. of calcium carbonate; or the solution contains calcium chloride equivalent to 10 parts of calcium carbonate per 70,000.

Run in the soap solution from a burette 1 c.c. at a time, shaking well after each addition. Continue the addition of the soap solution, but do not add more than 0·2 c.c. at a time as the end point is approached, as shown by the greater persistence of the lather. When the lather is permanent for five minutes, after the bottle has been laid on its side, the end point has been reached and the volume of the soap solution added is noted.

It will be observed that as the end point is approached the sound produced by shaking the bottle becomes less and less. This deadening effect on the sound affords a good means of determining the end point, especially if the water contains appreciable quantities of magnesium compounds, in which case a false lather may be obtained before the water is completely softened.

Repeat the experiment twice more and take the mean of the last two readings, which should not differ from one another by more than 0·3 c.c.

The soap solution must now be diluted so that 11 c.c. of it should be required to produce a permanent lather with

10 c.c. of the solution of calcium chloride and 60 c.c. of distilled water.

The 11 c.c. allows 10 c.c. for the calcium chloride and 1 c.c. for 70 c.c. of distilled water, as even if no calcium salt is in solution 1 c.c. of the standard solution of soap is required to produce a lather with 70 c.c. of distilled water.

Example :—

9·5 c.c. of soap solution were required for 10 c.c. $CaCl_2$ solution (1 c.c. = 0·001 gm. $CaCO_3$) and 60 c.c. of distilled water.

∴ 11 c.c. of soap solution should be made from 9·5 c.c. of original soap solution + 1·5 c.c. of a mixture of equal volumes of methylated spirit and water.

The amounts of the original soap solution and of the mixture of water and methylated spirit required to make 1 litre of the standard solution of soap are thus easily calculated.

If the soap solution is not approximately of the right concentration, it is advisable to add rather less than the calculated amount of solvent for the first dilution, as otherwise the solution may be found to be too weak after dilution.

If more than 11 c.c. of the original solution of soap were required in the experiment more soap should be added to the solution and the process of standardisation repeated.

When the soap solution has been adjusted repeat the titration to ascertain if exactly 11 c.c. of it are required for 10 c.c. of the calcium chloride solution and 60 c.c. of water. If slightly more or less than 11 c.c. is required, allowance must be made for this by using a factor for the solution in determining the hardness of the water under examination, but if less than 10 c.c. or more than 12 c.c. are required the solution should be restandardised.

The volume of this standard soap solution required for 70 c.c. of a sample of water, less 1 c.c., is taken to represent the number of degrees of hardness for that particular water, on the assumption that 1° of hardness represents 1 part of calcium carbonate per 70,000 of water, or 1 grain of calcium carbonate per gallon.

It should be noted, however, that the soap solution is standardised by means of a solution containing the equivalent of 10 parts of calcium carbonate per 70,000 which does not strictly represent a water having 10° of hardness (see p. 19).

Determination of the Total (Temporary and Permanent) Hardness of a Water.

Place 70 c.c. of the water under examination in a 200 c.c. glass-stoppered bottle and run in the soap solution until a permanent lather is obtained as described above. During the addition of the soap solution it is advisable to remove the carbon dioxide which is evolved owing to the decomposition of the calcium bicarbonate. This can be effected by attaching a glass tube to a filter pump and allowing the end of the tube to remain for a few seconds *above* the surface of the solution in the bottle.

The presence of carbonic acid delays the formation of the lather.

The volume of the soap solution required, which should be not more than 16 c.c., less 1 c.c., gives the number of degrees of total hardness of the water.

If more than 16 c.c. of the soap solution were required, the experiment should be repeated, using water which has been diluted with an equal volume of distilled water, and the degree of hardness obtained for this mixture should then be doubled to obtain the total hardness of the original water.

Determination of the Permanent Hardness by Standard Soap Solution.

Boil 250 c.c. of the water under examination in a flask for half an hour. Filter off the precipitated carbonates and collect the filtrate in a 250 c.c. flask. Rinse the flask in which the water was boiled with a little boiled distilled water. Cool and dilute to 250 c.c. with recently boiled,* cold distilled water.

Measure out 70 c.c. of the water from the 250 c.c. flask and titrate with the standard solution of soap. Repeat the titration twice and take the mean of the last two readings. Deduct 1 c.c. to obtain the number of degrees of permanent hardness. If more than 16 c.c. of the soap solution is required dilute the water as before. The difference between the permanent and total hardness gives the temporary hardness.

The degree of hardness of different waters varies very considerably according to the source of the waters, and, as would be expected, is usually in close relation to the total

* Recently boiled distilled water does not contain carbonic acid, which if present would redissolve some of the calcium carbonate.

solids contained in the water. Water having a total hardness of less than 5° is very soft, whilst if the total hardness is more than 20° the water will probably be found to be unsuitable for washing purposes.

The Action of Soap Solution on Water Containing Magnesium Salts in Solution.

It has been pointed out that if a water contains magnesium salts in solution a false lather may be obtained before the water is completely softened, as shown by the disappearance of the hard sound when the bottle containing the water and soap solution is shaken. In order to illustrate this phenomenon a solution containing only magnesium salt in quantity equivalent to the amount of calcium chloride used for standardising the soap solution should be made up, and the amount of soap solution required for softening the water noted.

1 gm. molecule of calcium carbonate should have the same soap-destroying power as 1 gm. molecule of magnesium sulphate, or

$$\underset{100 \text{ gms.}}{CaCO_3} \text{ corresponds to } \underset{246 \text{ gms.}}{MgSO_4 . 7H_2O}.$$

Make up a solution of magnesium sulphate containing 2·46 gms. of the crystallised salt per litre.

$$1 \text{ c.c. of this solution} = 0{\cdot}00246 \text{ gm. } MgSO_4 . 7H_2O$$
$$= 0{\cdot}001 \text{ gm. } CaCO_3,$$

so that 10 c.c. of the solution of magnesium sulphate + 60 c.c. of water gives a solution containing magnesium sulphate equivalent to 10 parts of calcium carbonate per 70,000, which was the concentration of the solution of calcium carbonate (in the form of calcium chloride) employed for the standardisation of the soap solution.

It will be remembered that 11 c.c. of the standard soap solution were required for 10 c.c. of the solution of calcium chloride + 60 c.c. of water. Find out by experiment how much of the standard soap solution is required to produce (1) a lather which is apparently permanent, (2) complete softening as shown by the disappearance of the sound on shaking, when a solution is employed containing 10 c.c. of the solution of magnesium sulphate and 60 c.c. of water.

It should be mentioned in this connection that if a soap containing only salts of *saturated* fatty acids be employed, the

volume of soap solution required to produce a permanent lather is the same, whether the solution contains calcium salts, or an equivalent amount of magnesium salts. (See H. Masters and H. L. Smith, "Trans. Chem. Soc.," 1913, **103**, 992.)

THE DETERMINATION OF THE HARDNESS OF WATER BY HEHNER'S METHOD.

Most natural waters are alkaline to methyl orange, and it is possible by titration of a given volume of the water with a standard solution of hydrochloric or sulphuric acid to determine the alkalinity of the water. Since the reaction is chiefly between the dissolved calcium carbonate (present as bicarbonate) and the acid, the determination of the alkalinity is usually referred to as a determination of *temporary* hardness, although as a rule there is no close agreement between the amount of calcium carbonate per 100,000 of the water as determined by this method and by means of a standard solution of soap.

It is also possible to obtain a measure of the *permanent* hardness of a water by finding out how much sodium carbonate is required for the precipitation of the calcium sulphate etc. present in a given volume of the water.

Determination of Temporary Hardness, or Alkalinity, of a Water by Titration with a Standard Solution of an Acid.

[Before proceeding with this experiment commence heating the water for the determination of permanent hardness, p. 26.]

A decinormal solution of hydrochloric acid is required.

From the equation

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

it will be seen that 73 gms. of hydrogen chloride, or 2000 c.c. N. HCl, decompose 100 gms. $CaCO_3$.

$\therefore$ 20,000 c.c. of N/10HCl decompose 100 gms. $CaCO_3$.

$\therefore$ 1 c.c. N/10HCl decomposes 0·005 gm. $CaCO_3$.

Thus if 500 c.c. of the water on titration in presence of methyl orange require 1 c.c. N/10HCl, 500 c.c. of the water contain 0·005 gm. $CaCO_3$, or 100,000 parts contain 1 part of $CaCO_3$.

Hence the number of c.c. of N/10 acid required for 500 c.c. of the water gives directly the number of parts of calcium carbonate per 100,000, that is the *temporary* hardness of the water.

Titrate three portions of 500 of the water under examination with N/10HCl, using methyl orange as indicator, and from the mean of the last two readings calculate the temporary hardness of the water.

Instead of titrating 500 c.c. of the water with N/10 acid, 100 c.c. may be employed if N/50 acid is used. The volume of acid required in this case will also give directly the parts of calcium carbonate per 100,000.

It should be noted that methyl orange is unaffected by the presence of carbonic or other very weak acid, so that the titration of the water in presence of this indicator may give an erroneous idea as to the absolute alkalinity or acidity of the water. As this is a matter of considerable importance in connection with the plumbosolvent action of a water, a method has been devised for the determination of the absolute acidity or alkalinity of a water. In this method solutions of disodium hydrogen phosphate, Na_2HPO_4, which contain hydroxyl ions in excess, and monopotassium hydrogen phosphate, KH_2PO_4, which contain hydrogen ions in excess, are mixed in known proportions. A mixture of the two solutions is prepared which gives the same colour with the indicator, azolitmin, as is obtained with this indicator and the water under examination. From the relative volumes of the two phosphate solutions required it is possible to determine not only whether the water contains hydroxyl or hydrogen ions in excess, but to obtain a measure of the excess of either. For details of the method see "Quantitative Analysis" by Cumming and Kay (Gurney & Jackson).

Determination of Permanent Hardness by Hehner's Method.

By boiling some of the water under examination with excess of a solution of sodium carbonate, all the hardness is removed, the temporary hardness by merely boiling and the permanent hardness by interaction of the calcium or magnesium sulphate with the sodium carbonate, with the precipitation of calcium or magnesium carbonate.*

* See, however, note on page 47.

In order to determine the permanent hardness, therefore, it is necessary to find out how much sodium carbonate is required by a given volume of water for this precipitation.

From the equation

$$CaSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CaCO_3$$

it will be seen that 1 gm. molecule of sodium carbonate is equivalent to 1 gm. molecule of calcium carbonate, i.e. 100 gms. $CaCO_3$.

1 gm. molecule of sodium carbonate is contained in 2 litres of N . Na_2CO_3 solution or 20,000 c.c. of N/10 sodium carbonate solution.

20,000 c.c. N/10Na_2CO_3 solution = 100 gms. $CaCO_3$.

Hence 1 c.c. N/10Na_2CO_3 solution is equivalent to 0·005 gm. $CaCO_3$, or, every c.c. of N/10Na_2CO_3 solution required for removal of the permanent hardness corresponds to 0·005 gm. $CaCO_3$ as permanent hardness.

It should be noted that although *permanent* hardness is due to the presence of calcium sulphate etc., it is expressed as parts of calcium carbonate per 100,000.

If 250 c.c. of water are employed for the test and if 1 c.c. of N/10Na_2CO_3 solution is required for removal of the permanent hardness, 250 c.c. of water contain calcium sulphate etc. equivalent to 0·005 gm. $CaCO_3$.

∴ 100,000 parts of water contain calcium sulphate etc. equivalent to $\frac{0{\cdot}005 \times 100{,}000}{250} = 2$ parts $CaCO_3$,

or each c.c. of N/10Na_2CO_3 solution required to remove the permanent hardness from 250 c.c. of water corresponds to 2 parts of $CaCO_3$ as permanent hardness.

Measure out 250 c.c. of the water under examination into a flask, add 50 c.c. of N/10 sodium carbonate solution and boil vigorously for half an hour.

Filter into a 250 c.c. graduated flask, wash with boiled distilled water and pour the washings through the filter paper. Cool the solution and dilute to 250 c.c. with distilled water.

Titrate 50 c.c. of the filtrate with N/10 hydrochloric acid, using methyl orange as indicator. Repeat the titration twice, and take the mean of the last two readings.

Calculate the volume of N/10 hydrochloric acid required for 250 c.c. of the solution.

Since 1 c.c. of N/10HCl = 1 c.c. N/10Na_2CO_3 solution, and 50 c.c. of N/10Na_2CO_3 were added to the 250 c.c. of water, 50 c.c. less the volume of N/10HCl used for the 250 c.c. of solution = volume of N/10Na_2CO_3 used for the removal of the permanent hardness from 250 c.c. of the water.

This volume × 2 = permanent hardness of the water, expressed as parts of $CaCO_3$ per 100,000 (see p. 27).

Example :—

250 c.c. of water were boiled with 50 c.c. N/10Na_2CO_3 solution for half an hour.

After filtering, washing the precipitate, cooling the solution and diluting to 250 c.c., 50 c.c. of the solution required 9·4 c.c. (mean) of N/10HCl.

∴ 250 c.c. would require 9·4 × 5 = 47·0 c.c.

∴ Volume of N/10Na_2CO_3 solution required for removal of the permanent hardness = 50 − 47 = 3 c.c.

1 c.c. N/10Na_2CO_3 solution = 0·005 gm. $CaCO_3$.

∴ 3 c.c. „ „ = 0·015 „ „

∴ In 250 c.c. of the original water the permanent hardness corresponds to 0·015 gm. $CaCO_3$.

∴ In 100,000 of the original water the permanent hardness corresponds to $\frac{0{\cdot}015 \times 100{,}000}{250} = 6$ parts of $CaCO_3$.

This result is also obtained, as indicated above, by multiplying the volume of the sodium carbonate solution by two.

THE ACTION OF WATER ON LEAD.

The action of water on lead is probably due to the presence of dissolved oxygen in the water. By the action of oxygen and water on the metal, lead hydroxide, $Pb(OH)_2$, is formed which is appreciably soluble in water,

$$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2.$$

Lead carbonate is less soluble in water than lead hydroxide, so that the presence of calcium bicarbonate in the water very largely prevents the continued action of the water on lead, owing to the formation of a protective layer of basic lead carbonate on the surface of the metal.

The question of the action of a natural water on lead is,

however, a complex one in view of the large number of factors involved, but owing to the poisonous nature of lead compounds and especially in view of the cumulative nature of the poison, the investigation of the action of water on lead is a matter of some considerable importance.

In order to illustrate the action of water on lead, place strips of freshly scraped lead foil in Nessler cylinders containing (*a*) distilled water, (*b*) water under examination, (*c*) distilled water to which a little sodium bicarbonate has been added. Allow these to remain in contact with the water for about a quarter of an hour. Remove the lead and test the waters for the presence of lead compounds by the addition of a little dilute acetic acid, to dissolve lead compounds in suspension, and a solution of sulphuretted hydrogen. A dark coloration due to the presence of lead sulphide will be obtained in *a* (distilled water), but probably not in *b* (water under examination) or *c* (distilled water to which sodium bicarbonate has been added).

The amount of lead taken up by a water under standard conditions can be determined by means of an apparatus described by Thresh *loc. cit.*

A very soft water (upland surface water from peat) often has a pronounced action on lead owing to the presence of organic acids in the water, and it is sometimes necessary to treat such a water with calcium carbonate to counteract this plumbosolvent action.

It should be noted that the action of water on lead is either of a solvent, or of an erosive nature, or of both. In the former case the lead compounds remain in solution, in the latter most of the lead compounds remain in suspension in the water.

The presence of sulphates and chlorides in a water often tends to increase its plumbosolvent action, as lead sulphate and chloride are more soluble than lead carbonate.

A water often has an initial action on new lead, but the surface of the metal rapidly becomes covered with a protective layer of a compound of lead and no further action is observed.

For further information as to the action of water on lead, see article on "Water" in Thorpe's "Dictionary of Applied Chemistry" (Longmans).

The Determination of Lead in Water.

In the absence of other metals which give a precipitate with sulphuretted hydrogen (see p. 31) this can be carried out

colorimetrically, by matching the colour obtained after the addition of a solution of sulphuretted hydrogen to a measured volume of the water after evaporation, with that obtained with a solution of lead acetate of known concentration.

Solutions Required :—

1. A solution of *lead acetate* of which

1 c.c. = 0·0001 gm. of lead.

From the relation

$$\underset{207}{Pb} : \underset{207 + 118 + 54}{Pb(CH_3COO)_2 . 3H_2O}$$

it will be seen that 207 parts of lead are contained in 379 parts of crystallised lead acetate.

$\therefore$ 0·0001 part of lead are contained in $\frac{379}{207} \times 0{\cdot}0001$

$= 0{\cdot}000183$ gm. of crystallised lead acetate.

$\therefore$ 1 litre of the solution required should contain 0·183 gm. of crystallised lead acetate, $Pb(CH_3COO)_2 . 3H_2O$.

Weigh out this amount of lead acetate, dissolve in recently boiled distilled water containing a few drops of acetic acid and dilute to 1 litre.

2. A freshly prepared aqueous solution of *sulphuretted hydrogen.*

Determination.—Evaporate 250 c.c. of the water under examination* to about 30 c.c.

Pour the water into a Nessler cylinder and wash the vessel twice with distilled water containing a little acetic acid to dissolve any lead carbonate which may have been formed. Pour the washings into the Nessler cylinder and dilute to 50 c.c.

Add 2 c.c. of the freshly prepared aqueous solution of sulphuretted hydrogen and stir the contents of the cylinder with a glass rod.

Into three other Nessler cylinders measure out 0·5, 1·0 and 1·5 c.c. of the standard solution of lead acetate. Dilute each solution to 50 c.c. and treat with 2 c.c. of sulphuretted hydrogen solution.

Compare the colours obtained with that obtained with the

* It is unlikely that the water under examination will contain lead. It is therefore advisable to add a measured volume, for example 1 c.c., of the standard lead acetate solution to 250 c.c. of distilled water and to determine the lead in this solution, in addition to carrying out the test on tap water.

water under examination, and vary the amount of the standard solution of lead acetate employed until the colours are exactly matched.

Each c.c. of the standard solution of lead acetate = 0·0001 gm. of lead, so that if 250 c.c. of original water require 1 c.c. of the standard solution for matching, 250 c.c. of water contain 0·0001 gm. lead.

$$\therefore \text{ 100,000 parts contain } \frac{0{\cdot}0001 \times 100{,}000}{250}$$

$$= 0{\cdot}04 \text{ part of lead.}$$

Calculate the amount of lead present per 100,000 of water.

In a water used for domestic purposes, in view of the cumulative nature of lead poisoning, this metal should be entirely absent.

In addition to its action on lead, a natural water often has a pronounced action on iron, copper and zinc. These metals may be tested for by the ordinary processes of qualitative analysis, after evaporation of a large volume of the water to a small bulk. The usual method, however, of distinguishing between small quantities of lead, copper and iron in water is to precipitate with colourless ammonium sulphide (prepared by passing sulphuretted hydrogen into a dilute solution of ammonia). The coloration due to ferrous sulphide is removed on addition of dilute hydrochloric acid, and that due to copper sulphide by the addition of a solution of potassium cyanide, whereas lead sulphide is unaffected by either treatment.

In the absence of lead, copper may be determined colorimetrically as cupric ferrocyanide, $Cu_2Fe(CN)_6$, and iron as ferric thiocyanate, $Fe(CNS)_3$.

OXYGEN DISSOLVED IN WATER.

In connection with water analysis a determination of the amount of oxygen *dissolved* in water is sometimes carried out. This determination is of importance in connection with the problem of the disposal of sewage.

The principle of the method is as follows :—

The water, after preliminary treatment to remove reducing agents, is treated with manganous chloride in presence of potassium hydroxide and potassium iodide. The manganous oxide is converted into a higher oxide of manganese by the oxygen present in the water, which then liberates iodine from

potassium iodide, the amount of which is determined by titration with a standard solution of sodium thiosulphate,

$$O \text{ (from oxide of manganese)} + 2KI + H_2O \rightarrow 2KOH + I_2.$$

From the amount of sodium thiosulphate solution required the amount of oxygen present in the water may be calculated. For details of the method see "The Examination of Waters and Water Supplies," by Thresh (Churchill).

Chapter II.

WATER-SOFTENERS AND "SODA" SUBSTITUTES.

"Alkali" in some form or other is used extensively for softening water and also as a detergent, both in laundry work and for various household purposes.

The form in which it is most usually employed is as "washing-soda" ($Na_2CO_3 . 10H_2O$), but preparations of water-softeners and soda substitutes can now be obtained in great variety.

A chemical analysis of such preparations is of great value in determining how far they are suitable for the purposes for which they are sold.

Sodium carbonate is as a rule the chief constituent of such preparations, and on examination they are usually found to contain one or more of the following substances :—

Sodium Carbonate (Na_2CO_3), either anhydrous or in various hydrate forms such as: $Na_2CO_3 . H_2O$ (crystal carbonate); $Na_2CO_3 . 5H_2O$; $Na_2CO_3 . 7H_2O$; $Na_2CO_3 . 10H_2O$ (washing-soda); and $Na_2CO_3 . NaHCO_3 . 2H_2O$ (sodium sesquicarbonate).

Sodium Bicarbonate ($NaHCO_3$).

Sodium Silicate (Na_2SiO_3), usually present in a hydrated form.

Borax ($Na_2B_4O_7 . 10H_2O$), sometimes also sodium perborate ($NaBO_3 . 4H_2O$).

Caustic Soda (NaOH), not often found, since even if originally present it is rapidly converted into $NaHCO_3$ on exposure to atmospheric carbon dioxide.

Ammonia (NH_4OH), in solutions only.

The reactions of the substances mentioned above have already been dealt with in the ordinary course of qualitative analysis, but before undertaking the examination of a water softener it is advisable to make a rather more detailed study of the reactions of these alkalis.

Reactions of the Common Alkalis.

Prepare a solution in water of each of the above-mentioned alkalis, treat portions of each solution with the following reagents (using a fresh portion of solution for each test): (*a*) hydrochloric acid, (*b*) silver nitrate, (*c*) mercuric chloride, and note the following reactions :—

Reagent.	Substance to be Tested.				
	Caustic Soda.	Sodium Carbonate.	Sodium* Bicarbonate.	Borax.	Sodium Silicate.
Hydrochloric acid.	—	Evolution of CO_2.	Evolution of CO_2.	See note (3).	Gelatinous precipitate of H_2SiO_3 (1).
Silver nitrate.	Brown precipitate.	White precipitate.	White precipitate.	White precipitate turning brown on heating (2).	White precipitate.
Mercuric chloride.	Yellow precipitate.	Red-brown precipitate of basic salt.	No precipitate at first, red-brown on standing.	Red-brown precipitate.	Red-brown precipitate.

Note.—(1) The solution of the silicate should be moderately strong and a few drops of concentrated hydrochloric acid should be added.

(2) A white precipitate of silver metaborate ($AgBO_2$) is first formed, which on heating, or on considerably diluting with water, becomes hydrolysed with the formation of silver oxide (Ag_2O).

(3) If hydrochloric acid is added to a *concentrated* solution of borax a white precipitate of boric acid is obtained, but in more dilute solutions the boric acid is not precipitated.

The following reactions should also be carefully noted :—

Reactions of Carbonates and Bicarbonates.—A solution of sodium bicarbonate, made in the cold, gives off carbon dioxide on heating—(test for the presence of this gas with lime water). On the addition of magnesium sulphate to a solution containing a carbonate a white precipitate of basic magnesium

* Solutions which are to be tested for bicarbonate should always be made in the *cold*, since on heating the following reaction takes place :—

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

carbonate is obtained immediately, but on the addition of magnesium sulphate to a solution containing sodium bicarbonate no precipitate is obtained until the solution is boiled.

It should be noted that solutions containing both carbonate and bicarbonate usually give a red-brown precipitate with mercuric chloride (indicating the presence of carbonate) and no precipitate with magnesium sulphate until the solution is boiled (indicating the presence of bicarbonate).

Reactions of Sodium Silicate.—A gelatinous precipitate (H_2SiO_3) is obtained on the addition of ammonium chloride to a solution of sodium silicate, the precipitate being often more readily obtained by this means than by the addition of hydrochloric acid.

In this reaction the ammonium silicate first formed is hydrolysed by the action of water giving ammonia and silicic acid thus

$$Na_2SiO_3 + 2NH_4Cl \rightarrow (NH_4)_2SiO_3 + 2NaCl$$
$$(NH_4)_2SiO_3 + 2H_2O \rightarrow H_2SiO_3 + 2NH_4OH.$$

As a confirmatory test a portion of the solution should be evaporated to dryness with hydrochloric acid and the formation of an insoluble residue (SiO_2) noted.

Reactions of Borates.—In addition to the reactions given above the presence of borate is indicated by the following tests :—

(1) Acidify the solution with hydrochloric acid, dip a piece of turmeric paper into the solution and carefully dry the paper. In the presence of a borate the paper turns orange-brown and this colour changes to bluish-green when the paper is moistened with sodium hydroxide or ammonia. The test may also be made using an alcoholic solution of turmeric as in testing for boric acid in milk (see Vol. II.).

(2) Mix some borax with a few drops of concentrated sulphuric acid and a little alcohol in a porcelain dish. Ignite the alcohol and observe that the flame becomes tinged with green.

Ammonium Hydroxide.—Ammonia is usually detected by its smell and by the fact that the solution on heating gives off a gas which turns moistened red litmus paper blue and turmeric paper brown.

METHODS OF EXAMINING WATER-SOFTENERS AND SODA SUBSTITUTES.

These preparations are usually obtained in the form of lumps or powder, which dissolve readily in water. A small amount of insoluble matter, chiefly grit etc., is sometimes present; this should be filtered off and the filtrate then tested as described below.

Other preparations, sold as "cleansers" and "scourers," often contain a considerable amount of grit and sometimes soap in addition; these, however, will be dealt with later (see p. 74).

A portion of the substance (if a solid) should be dissolved in water or, if a liquid, diluted with water and portions of the solution treated with (*a*) hydrochloric acid, (*b*) silver nitrate, (*c*) mercuric chloride. This, as indicated above, should give some idea as to the nature of the alkali or alkalis present.

If carbonate is present further tests should be made in order to ascertain whether the normal carbonate or the bicarbonate, or both, are present.

Portions of the solution should also be tested for borate and silicate.

If the substance is stated to have bleaching properties some oxidising agent, e.g. perborate or sodium peroxide may be present.

In this case a portion of the solution should be acidified with dilute sulphuric acid and a few drops of a dilute solution of potassium permanganate added. If the permanganate is decolorised an oxidising agent is present. If borate is also found it may be assumed that perborate is present, but this subject is dealt with more fully under "Bleaching Agents," page 149.

In addition to the alkaline substances already dealt with, water softeners sometimes contain small quantities of neutral salts, e.g. chloride and sulphate.

Portions of the solution should therefore be tested for the presence of these substances.

Quantitative Examination of "Water Softeners" and "Soda-Substitutes".

It is impossible to obtain any real comparison of the relative merits of various preparations under consideration unless some

information is obtained as to the quantities of the principal constituents present.

A qualitative analysis on the lines indicated above should first be made, and the quantities of the principal constituents present can then be determined by the ordinary processes of quantitative analysis.

The methods to be used will, of course, vary with the nature of the substances present, but since, as already pointed out, such preparations usually contain sodium carbonate, either alone or in addition to one or more of the alkalis mentioned above (p. 33), the determinations can, as a rule, be carried out in the following manner:—

Weigh out accurately 2-3 gms. of the substance, dissolve in water, filter off any insoluble matter, and dilute to 250 c.c. in a graduated flask.

Determination of Sodium Carbonate.—If the substance contains sodium carbonate only, titrate 25 c.c. of the solution with decinormal acid (using methyl orange as indicator) and calculate the percentage of sodium carbonate present in the substance. (1 c.c. N/10 acid = 0·0053 gm. Na_2CO_3.)

Determination of Sodium Carbonate and Sodium Bicarbonate.—If both sodium carbonate and bicarbonate are present the quantity of each present may be determined by titrating 25 c.c. of the solution with decinormal acid, using first phenolphthalein and then methyl orange as indicator.

It should be remembered that phenolphthalein gives a pink coloration with normal sodium carbonate, but not with sodium bicarbonate.

The method depends upon the fact that when sodium carbonate is acted upon by acids the neutralisation takes place in two stages—

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3 \quad \text{1st stage.}$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2 \quad \text{2nd stage.}$$

When half the volume of acid required for complete neutralisation of the carbonate is added the sodium carbonate is entirely converted into bicarbonate. If, therefore, a solution containing sodium carbonate and sodium bicarbonate is titrated with decinormal acid, using phenolphthalein as indicator, the disappearance of the pink colour will show when *half* the volume of acid required to neutralise the sodium carbonate has been added.

If methyl orange be then added and the titration continued

until all the alkali present has been neutralised, this second titration gives a measure of the volume of acid required to complete the neutralisation of the carbonate (i.e. half the volume required for complete neutralisation) together with that required for the neutralisation of the bicarbonate originally present.

Since the volume of acid required to half-neutralise the carbonate is given by the first titration, the volume of acid required for the neutralisation of the bicarbonate is obtained by difference, and is equal to the volume of acid required for the second stage of the neutralisation, less that required for the first. It is also equal to the total volume of acid required for neutralisation, less twice that required for the first stage.

This method in which two indicators are employed is not one of very great accuracy, since the disappearance of the pink colour of the phenolphthalein on the conversion of the carbonate to bicarbonate does not form a very sharp end point. If certain precautions are taken, however, the method gives results of quite sufficient accuracy for most practical purposes.

The acid should be run in slowly and well mixed with the solution so as to avoid any local excess of acid, or some of the sodium carbonate may become completely neutralised, with the consequent liberation of carbon dioxide during the first stage of the titration, and inaccurate results will be obtained. For this reason also the titration is best carried out in a dish, the contents of which are kept well stirred with a glass rod. The tip of the burette should be lowered close to the surface of the liquid, and the acid should be run in slowly down the glass rod so as to avoid any splashing and the consequent liberation of carbon dioxide.

The following example shows the method of calculation :—

2·5 gms. of a powder containing sodium carbonate and sodium bicarbonate were dissolved in water and the solution made up to 250 c.c.

25 c.c. of the solution were titrated with decinormal acid.

Volume of acid required to discharge pink colour of phenolphthalein = 8·5 c.c. N/10 acid.

Methyl orange was then added and the volume required to complete neutralisation = 18·6 c.c. N/10 acid.

Volume of acid required to neutralise sodium carbonate in 25 c.c. solution = 8·5 × 2 = 17·0 c.c.

Volume of acid required to neutralise sodium bicarbonate in 25 c.c. solution = 18·6 − 8·5 = 10·1 c.c.,
or total acid 27·1 c.c. less 2 × 8·5 = 10·1 c.c.

From the equations

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$$
106 gms. 98 gms.
53 ,, 49 ,, (or 1 litre of N . H_2SO_4)

and $$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2$$
2 × 84 gms. 98 gms.
84 ,, 49 ,, (or 1 litre of N . H_2SO_4)

it will be seen that,

1 c.c. of N/10 acid = 0·0053 gm. sodium carbonate
and 1 c.c. ,, ,, ,, = 0·0084 ,, ,, bicarbonate.
∴ Weight of sodium carbonate in 25 c.c. solution
= 17·0 × 0·0053 gms.
or weight of sodium carbonate in 250 c.c. solution
= 17·0 × 0·0053 × 10 gms.
∴ Weight of sodium carbonate in 2·5 gms. powder
= 17·0 × 0·0053 × 10 gms.
Weight of sodium carbonate in 100 gms. powder
= 17·0 × 0·0053 × 10 × 40
= 36·0 gms.

Similarly weight of sodium bicarbonate in 100 gms. powder

$$= 10{\cdot}1 \times 0{\cdot}0084 \times 10 \times \frac{100}{25}$$

= 33·9 gms.

Quantitative Analysis of Mixtures Containing Carbonate, Borate and Silicate.

If sodium silicate or borate, or both, are present in addition to sodium carbonate the total alkalinity should be determined as Na_2O, by titrating 25 c.c. of the solution (prepared as described on p. 37) with decinormal acid, using methyl orange as indicator.

From the equation

$$Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$$
62 gms. 98 gms.
31 ,, 49 ,,

it will be seen that 1 c.c. N/10 acid = 0·0031 gm. Na_2O.

The quantities of SiO_2, B_2O_3 and CO_2 present can then be

determined by the ordinary processes of quantitative analysis as described below.

Determination of Silica (SiO_2).—Weigh out accurately about 1 gm. of the substance into a porcelain dish and moisten with water.* Place the dish, covered with a clock glass, on a water bath; then gradually add concentrated hydrochloric acid through a small opening, left by drawing aside the clock glass, and stir the contents of the dish with a glass rod.

As soon as the powder is completely decomposed, which is known to be the case when no gritty particles can be felt with the rod, remove the clock glass, wash it with distilled water, allow the washings to fall into the dish and evaporate the solution to dryness. Stir the residue well and when quite dry add more hydrochloric acid and again evaporate to dryness.

Add hot water to the residue, stir well, allow the solid to subside and decant the liquid through a filter.

Wash the residue (SiO_2) two or three times by decantation, then transfer it to the filter, wash with hot water, dry and ignite.

From the weight of silica thus found the percentage of silica may be calculated.

Determination of Boric Anhydride (B_2O_3).—When sodium hydroxide is added to a solution of boric acid the acid is partially converted into sodium metaborate ($NaBO_2$). Sodium borate is, however, appreciably hydrolysed in solution, and the reaction is therefore a reversible one and may be represented thus :—

$$H_3BO_3 + NaOH \rightleftharpoons NaBO_2 + 2H_2O.$$

For this reason free boric acid cannot be titrated by itself, but if a sufficient quantity of glycerol (or mannitol) is added to the solution, hydrolysis is prevented, and when sodium hydroxide in excess of that required to neutralise the boric acid is added (1 molecule NaOH is equivalent to 1 molecule H_3BO_3), the solution, in the presence of phenolphthalein, changes from colourless to pink.

This method only gives accurate results when the solution is absolutely free from carbonate. In the case of mixtures

* If the powder contains insoluble matter, i.e. grit, it should be dissolved in water and the solution filtered to remove the grit. The residue should be washed with hot water and the filtrate and washings evaporated to dryness with hydrochloric acid, as described.

containing both carbonate and borate the determination can, however, be satisfactorily carried out as follows:—

Determine the total amount of alkali present (as described on p. 39) by titrating 25 c.c. of the solution with decinormal acid. Boil the neutralised solution for a few minutes to expel carbon dioxide,* cool and add decinormal caustic soda until the pink colour of the methyl orange (a little more of which should be added if necessary) just assumes a pure yellow tinge. At this stage boric acid will exist in a free state.

Add glycerol in such proportion that the total solution after titration will contain at least 30 per cent.,† then add a few drops of phenolphthalein and titrate with decinormal caustic soda until a pink coloration is produced.

This gives the volume of decinormal soda solution required to neutralise the boric acid, and from this the percentage of the acid can be found.

From the equations

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3, \quad 2H_3BO_3 + 2NaOH \rightarrow 2NaBO_2 + 4H_2O$$

70 gms. 2×62 gms. 2×40 gms.

35 „ 62 „ 40 „ (or 1 litre. N. NaOH)

it will be seen that

$$1 \text{ c.c. of } N/10 NaOH = 0{\cdot}0062 \text{ gm. } H_3BO_3$$
$$= 0{\cdot}0035 \text{ gm. } B_2O_3.$$

Determination of Carbon Dioxide.—When a carbonate is acted upon by dilute acid, carbon dioxide is given off, and the quantity of carbon dioxide present may be found by determining the loss in weight of the substance during the reaction. This process may be conveniently carried out in the apparatus shown in the diagram, Fig. 3.

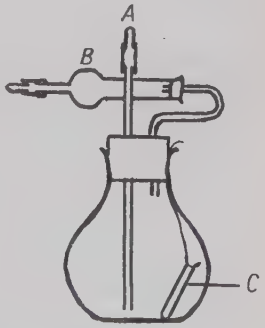


FIG. 3.

It consists of a small wide-necked flask fitted with a two-holed rubber stopper. The stopper carries a straight glass tube A which passes nearly to the bottom of the flask and a small calcium chloride tube B. The ends of these tubes

* Boric acid is slightly volatile in steam, therefore prolonged boiling should be avoided otherwise some of the boric acid will be lost.

† If mannitol is used instead of glycerol 1·5 to 2 gms. of the former may replace 50 c.c. of the latter.

are fitted with short pieces of rubber tubing, which are closed with small lengths of glass rod with rounded ends.

The dilute sulphuric acid required for the decomposition of the carbonate is placed in a small tube C, which is held obliquely by the *thin* thread supporting it.

The empty flask is first weighed.

Weight of flask = W_1.

About 1 gm. of the solid is introduced into the flask and the flask again weighed = W_2.

Then $W_2 - W_1$ = weight of substance used for experiment.

The small tube is filled with dilute sulphuric acid, and the apparatus then fitted up ready for use, as shown in the diagram, and weighed (without the caps).

Weight of apparatus ready for use = W_3.

The tube A is then closed by means of the cap and the acid is caused to flow over the carbonate by tilting the flask, so as to cause a gradual evolution of carbon dioxide. When all the acid has been poured from the tube and the effervescence has ceased, the flask is warmed. The cap on A is removed and a slow stream of air is drawn through the flask and drying tube (by means of a water pump attached to the calcium chloride tube B) to displace the carbon dioxide.

The tubes A and B are then closed by means of the caps and the apparatus when quite cold is weighed again (without the caps).

Weight of apparatus after the experiment = W_4.

Then $W_3 - W_4$ = loss in weight of apparatus due to the evolution of CO_2; or, the weight of CO_2 evolved from $W_2 - W_1$ gm. of powder. From this the weight of CO_2 evolved from 100 gms. can be calculated.

Determination of Carbon Dioxide by Means of a Nitrometer.—The percentage of carbon dioxide can also be determined by measuring the volume of gas evolved on treatment with dilute acid.

This process may be carried out in a Lunge Nitrometer.

Lunge Nitrometer.—A diagram of the apparatus is shown in Fig. 4. It consists of a measuring tube A graduated from 0-50 c.c. and fitted at the top with a two-way tap B, by means of which A can be connected either with the funnel F,

which is open to the air, or with the capillary side tube C to which is attached, by means of a piece of rubber pressure tubing, the flask D containing a small glass tube E. D and E together contain all the necessary reagents for generating the gas of which the volume is to be measured.

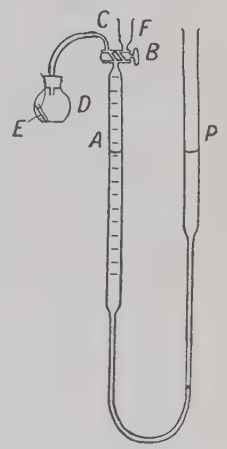


FIG. 4.

The other end of the measuring tube A is connected by a flexible rubber tube with a glass tube P, known as the pressure tube.

To fill the nitrometer with mercury or other suitable confining liquid * turn B so that A is open to the air; pour the liquid into the pressure tube P and raise this tube until the liquid fills A. Then adjust the height of P so that the liquid is at the same level in both tubes and stands at about the 1 c.c. mark in A. Close the tap B.

If mercury is used as the confining liquid the apparatus must be supported over a mercury tray.

Note.—The nitrometer is graduated to measure 50 c.c. of gas and the amount of substance used should be such that not more than 30-40 c.c. of gas are given off under ordinary atmospheric conditions.

The equation

$$\underset{106\text{ gms.}}{Na_2CO_3} + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + \underset{\substack{44\text{ gms.}\\(22{\cdot}4\text{ l. at N.T.P.})}}{CO_2}$$

shows that 106 gms. of anhydrous sodium carbonate would liberate 22·4 *litres* of gas (at N.T.P.) or 0·106 gm. would liberate 22·4 c.c. So that in the case of a preparation which contains only a proportion of sodium carbonate, 0·2-0·5 gm. should yield a volume of gas which can be conveniently measured in the nitrometer.

If this quantity is found to give only a small reading another experiment using a larger quantity should be made.

To Determine the Amount of Carbon Dioxide in a "Water-Softener".—Fill the nitrometer with brine. Weigh the flask

* *Confining liquid.*—The confining liquid which should be used depends on the nature and solubility of the gas to be collected. For carbon dioxide brine should be used, as the gas is less soluble in this than in water.

D, introduce a small quantity of the powder, 0·2-0·5 gm., into the flask and weigh again.

Fill the small tube T with dilute sulphuric acid and suspend in D by a *thin* thread, so that it stands obliquely in the flask without touching the stopper and without slipping into a horizontal position (see Fig. 4). Attach the flask D to the capillary tube C by means of the rubber pressure tubing.

Turn B so as to connect D with A. As a rule, owing to a slight compression of the air in D, the level of liquid in A falls through a short distance. In this case adjust the height of P until the level of liquid in the two tubes is again the same; the air in D will then be at atmospheric pressure.

Read the level of the liquid in A.

In order to test whether the apparatus is gas tight, lower the pressure tube P so that there is a difference of about eight inches between the level of the liquid in this tube and that of the liquid in the tube A. After about two minutes raise the tube P so that the level of the water in it is the same as that in the tube A. If the apparatus is gas tight, the volume of air in A will be the same as before. If this is the case, lower the tube P slightly and tilt the flask D gently so as to bring the acid into contact with the powder. As the gas is evolved gradually lower P, so that the level of the liquid in this tube is always slightly lower than the level of the liquid in A; in this way unnecessary pressure in the apparatus is avoided.

When the reaction is complete (i.e. no further alteration of the level of the liquid in A is observed) raise P until the level of the liquid in the two tubes is again the same and allow the apparatus to stand for about half an hour, in order to ensure that the gas is at room temperature.

Read off the volume of the gas in A, after finally adjusting the levels of the liquid in A and P. This reading, minus the first reading, gives the volume of gas evolved during the reaction, measured at atmospheric temperature and pressure.

Note the barometric pressure and the room temperature and correct the volume of gas to 0° C. and 760 mm. pressure.

Calculate the weight of this volume of carbon dioxide, and hence find the percentage of carbon dioxide liberated from the powder.

Example.—0·30 gm. of a water-softener gave 30·6 c.c. of carbon dioxide measured at 761 mm. pressure and 17° C.

(The tension of aqueous vapour at 17° C. = 14·4 mm.)

The volume of gas corrected to 0° C. and 760 mm. pressure

$$= 30{\cdot}6 \times \frac{273}{273+17} \times \frac{761 - 14{\cdot}4}{760}$$

$$= 30{\cdot}6 \times \frac{273}{290} \times \frac{746{\cdot}6}{760}$$

$$= 28{\cdot}3 \text{ c.c.}$$

Since 22·4 litres of CO_2 at N.T.P. weigh 44 gms.

22·4 c.c. ,, ,, ,, ,, 0·044 gm.

Thus the weight of carbon dioxide liberated from 0·3 gm. of powder $= \frac{28{\cdot}3 \times 0{\cdot}044}{22{\cdot}4}$,

and the weight of carbon dioxide in 100 gms.

$$= \frac{28{\cdot}3 \times 0{\cdot}044 \times 100}{22{\cdot}4 \times 0{\cdot}3} = 18{\cdot}5 \text{ gms.}$$

The powder contains 18·5 per cent. of carbon dioxide.

Determination of Moisture.—If the substance is a solid the percentage of water present can be determined in the usual manner, i.e. by weighing out 2-5 gms. of the substance and drying to constant weight over a burner.

It should be noted that if sodium bicarbonate is present, there will be a loss in weight on drying due to its conversion into sodium carbonate, and unless a correction is applied this loss will be returned as moisture.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

$$2 \times 84 \qquad\qquad 18 + 44$$

$$2 \times 84 \qquad\qquad 62$$

$$84 \qquad\qquad 31$$

Thus on 84 gms. of sodium bicarbonate there would be a loss on heating of 31 gms.

Hence if the percentage of sodium bicarbonate has already been determined (see p. 37), this figure multiplied by $\frac{31}{84}$ will give the correction which should be subtracted from the percentage loss on drying, in order to obtain the percentage of moisture in the powder.

Discussion of the Results.

A discussion as to the relative suitability of the different alkalis for laundry and other purposes will be dealt with in the course of lectures.

It may, however, be noted here that no universal water-softener can be considered satisfactory, since the nature and quantity of the reagents used for softening should depend, as shown below, on the type of water to be dealt with, and also that preparations containing considerable quantities of sodium silicate are unsuitable for laundry work.

** CALCULATIONS AND EXPERIMENTS RELATING TO THE SOFTENING OF WATER.

As the gallon is still used as the standard measure of volume in most laundries, it is convenient for this purpose to express the hardness in terms of grains of calcium carbonate per gallon, and to regard one degree of hardness (1°) as that due to 1 grain of calcium carbonate, or its equivalent of any other calcium or magnesium salt, dissolved in one gallon of water.

The agencies which may be considered to be available for the process of softening in laundry practice are heat, addition of lime, caustic soda, sodium carbonate and mixtures of the last three.

Heat.—The application of heat only removes the temporary hardness. The dissolved carbon dioxide is removed by boiling and the calcium or magnesium bicarbonate originally present is precipitated as the insoluble carbonate thus :—

$$CaCO_3 . H_2CO_3 \rightarrow CaCO_3 + H_2O + CO_2.$$

On a large scale, heat is as a rule out of the question on the score of expense, and one or more of the above-mentioned substances must be employed. To ensure good results with economy, the principles on which the application of these substances is based should be clearly understood.

Lime.—Lime removes the temporary hardness by neutralising the dissolved carbonic acid, thus converting the soluble calcium or magnesium bicarbonate into insoluble calcium carbonate thus :—

$$\underset{100}{CaCO_3 . H_2CO_3} + \underset{\substack{CaO . H_2O \\ 56 + 18}}{Ca(OH)_2} \rightarrow 2CaCO_3 + 2H_2O.$$

Hence water which has only temporary hardness may be softened by the addition of lime either in the form of slaked lime or lime water.

The solubility of lime in water is only about 1 part in 700,

and this involves the use of relatively large volumes of the solution which is often inconvenient in practice.

For this reason the lime is usually made up to a milk with a small quantity of water and added in this form.

From the equation given above it will be seen that 100 parts of calcium carbonate, present as bicarbonate, will require 56 parts of quicklime (CaO) or 74 parts of slaked lime ($Ca(OH)_2$), and if the temporary hardness of the water has been determined the amount of lime which should be added can easily be calculated.

In practice it is not possible to realise such a perfect reaction as is represented by the equation, and with most waters more lime will be required than is indicated by the temporary hardness, as there is in nearly all cases a larger amount of carbonic acid than that which is necessary to hold the carbonates of calcium and magnesium in solution.

A preliminary experiment should be made using the amount of lime indicated by calculation from the temporary hardness, and if the softening thus effected is found to be insufficient a further trial, using a larger proportion of lime, can be made.

*Sodium Carbonate.**—The addition of lime leads only to the removal of the temporary hardness, and when water is hard from the presence of calcium sulphate or chloride the proper softening agent to use is sodium carbonate, the reaction being represented thus :—

$$\underset{136}{CaSO_4} + \underset{106}{Na_2CO_3} \rightarrow CaCO_3 + Na_2SO_4$$

(= 100 of $CaCO_3$).

Calcium carbonate is precipitated and the sodium sulphate remains in solution.

From the equation it will be seen that 100 parts of the calcium salt in terms of carbonate will require 106 parts of sodium carbonate.

* *Sodium Carbonate.*—Although sodium carbonate is usually employed to remove permanent hardness, it will also react with calcium bicarbonate as shown in the following equation :—

$$CaCO_3 . H_2CO_3 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3.$$

On heating, the bicarbonate decomposes, forming carbonate :—

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

The water is thus left alkaline from the presence of sodium carbonate (and bicarbonate) and this is a disadvantage if the water is to be used for the washing of woollen and silk goods. (See pp. 91 and 97 for action of alkalis on silk and wool.)

Testing with soap solution after softening will show whether the hardness has been satisfactorily removed, but will not indicate whether too much sodium carbonate has been added, and for this reason it is advisable to determine the alkalinity of the water before and after softening.

Caustic Soda.—Caustic soda behaves like lime with regard to temporary hardness, but in this case sodium carbonate is formed and is thus available to react with the substances present in the water which give rise to permanent hardness.

$$\underset{100}{CaCO_3 . H_2CO_3} + \underset{80}{2NaOH} \rightarrow CaCO_3 + \underset{106}{Na_2CO_3} + 2H_2O$$

$$\underset{136}{CaSO_4} + \underset{106}{Na_2CO_3} \rightarrow CaCO_3 + Na_2SO_4$$

(= 100 of $CaCO_3$).

If, therefore, the two forms of hardness are in about equal proportions the addition of an appropriate amount of caustic soda would effect a satisfactory softening.

The equations show that:—

100 parts of calcium carbonate will require 80 parts of caustic soda, and this will produce sufficient sodium carbonate to remove 100 parts of permanent hardness (expressed as $CaCO_3$).

Here again it should be remembered that the water will probably contain excess of carbon dioxide, and a trial experiment should be made in order to see if further softening can be effected, by using a little more caustic soda than the amount theoretically indicated, without appreciably increasing the alkalinity of the water.

This method of softening has the advantage that the deposit obtained is less bulky than when lime is used, and if the water has to be filtered after softening it may be inconvenient to deal with a large amount of solid matter.

SUMMARY OF METHODS OF SOFTENING WATER. REMOVAL OF TEMPORARY AND PERMANENT HARDNESS.

The most suitable softening agent to employ and the proportions of reagents to be used depend on the degree of hardness of the water and the relative amounts of temporary and permanent hardness.

Waters also vary in the character of the deposit given with softening agents, and whether this settles or filters easily

will be found frequently to depend on the nature of the softener used. So far as this particular point is concerned each water must be treated on its own merits, but the general principles guiding the choice and application of softening agents for waters exhibiting mixed hardness may be briefly summarised here.

(*a*) The Use of Lime and Sodium Carbonate.

A water containing both temporary and permanent hardness can be softened by adding lime equivalent to the temporary hardness together with sodium carbonate equivalent to the permanent hardness.

(*b*) The Use of Caustic Soda.

As already indicated (see p. 48) if the temporary and permanent hardness are present in about equal proportions the water may be conveniently softened by the use of caustic soda.

Caustic soda equivalent to the temporary hardness should be added, and this will furnish sufficient sodium carbonate to remove an equivalent amount of permanent hardness.

(*c*) The Use of Lime and Caustic Soda.

A water in which the temporary hardness exceeds the permanent hardness can be softened by adding caustic soda equivalent to the permanent hardness, and lime equivalent to the difference between the temporary and permanent hardness.

The temporary hardness removed by the action of the caustic soda will be equivalent in amount to the permanent hardness and the excess of temporary hardness will be removed by the lime.

(*d*) The Use of Caustic Soda and Sodium Carbonate.

A water in which the permanent hardness exceeds the temporary hardness can be softened by adding caustic soda equivalent to the temporary hardness and sodium carbonate equivalent to the difference between the permanent and temporary hardness.

The amount of permanent hardness removed by the sodium carbonate will be equivalent to the temporary hardness, and

the excess of permanent hardness will be removed by the additional sodium carbonate.

With a water of this type it is advisable to make a trial experiment, using caustic soda alone, in slight excess, as unless the permanent hardness greatly exceeds the temporary hardness, it is possible that the excess of carbonic acid when neutralised with caustic soda will furnish sufficient carbonate to remove this excess of permanent hardness (see p. 48).

Degree of Softening.

Water which is to be used for laundry purposes only cannot be too soft, but the cost of removing the hardness completely may exceed the loss due to waste of soap caused by moderate hardness, and softening down to between 4° and 6° may be considered as far as it is practicable to go with due regard for economy.

CALCULATION OF THE QUANTITIES OF REAGENTS REQUIRED FOR SOFTENING A GIVEN VOLUME OF WATER OF KNOWN DEGREE OF HARDNESS.

Since by definition, 1° of hardness = 1 grain of calcium carbonate (or its equivalent) in 1 gallon, the number of grains of calcium carbonate present in any given number of gallons of water may be taken as the product of the number of gallons and the degrees of hardness. (See, however, p. 19.)

For example, 10 gallons of a water of 12° of hardness will contain 12 × 10 = 120 grains of calcium carbonate (or its equivalent).

The equations given on pages 46-48 show that 1 grain of calcium carbonate is equivalent to

0·56 grain CaO,
or 0·8 „ NaOH,
„ 1·06 „ Na_2CO_3.

Thus,

grains of $CaCO_3$ × 0·56 = grains of lime required to soften the water
„ „ × 0·8 = „ „ caustic soda required to soften the water
„ „ × 1·06 = „ „ sodium carbonate required to soften the water.

Example.

Calculation of the amounts of reagents required to soften 10 gallons of water having 14° of temporary hardness and 6° of permanent hardness :—

(*a*) *With Lime and Sodium Carbonate.*—Add lime equivalent to the temporary hardness and sodium carbonate equivalent to the permanent hardness (see p. 49 (*a*)).

The temporary hardness = 14° = 14 grains in 1 gallon
= 140 „ „ 10 gallons.
Quantity of lime required = 140 × 0·56 grains
= 78·4 grains.
The permanent hardness = 6° = 6 grains in 1 gallon
= 60 „ „ 10 gallons.
Quantity of sodium carbonate required = 60 × 1·06 grains
= 63·6 grains.

(*b*) *With Lime and Caustic Soda.* — Add caustic soda equivalent to the permanent hardness and lime equivalent to the difference between the temporary and permanent hardness (see p. 49 (*c*)).

The permanent hardness = 6° = 6 grains in 1 gallon
= 60 „ „ 10 gallons.
Quantity of caustic soda required = 60 × 0·8 grains
= 48 grains.
Temporary *minus* permanent hardness = 14° − 6° = 8°
= 8 grains in 1 gallon
= 80 „ „ 10 gallons.
Quantity of lime required = 80 × 0·56 grains
= 44·8 grains.

To Convert Grains to Grams.—In the laboratory it will be found more convenient to express the result in grams instead of grains.

1 gram = 15·4 grains.

$$\text{Hence, grains} \times \frac{1}{15{\cdot}4} (= 0{\cdot}065) = \text{grams.}$$

Experiments on the Softening of Water.

In carrying out experiments on water-softening it is advisable, if satisfactory results are to be obtained, to work with a fairly large quantity of water, e.g. 10 gallons.

To soften 10 gallons of water for laundry purposes proceed in the following manner:—

Determine the temporary and permanent hardness of the water by means of a standard soap solution as described on page 23.

Determine also the alkalinity of the water (Hehner's Method, p. 25).

Measure out 10 gallons of the water into a suitable containing vessel.

I. *To Soften with Lime and Sodium Carbonate.*—Calculate as shown above the number of grains of lime and the number of grains of sodium carbonate required. Convert grains to grams and weigh out the necessary quantities.

Mix the lime to a smooth paste with water, thin down with more water and pour into the 10 gallons of water to be softened.

Add the sodium carbonate dissolved in a small quantity of water. Stir well and leave the water to stand for several hours until the precipitate has settled.

Draw off a sample of water from the top without disturbing the precipitate.

Determine the temporary and permanent hardness, also the alkalinity.

If the softening is found to be insufficient, repeat the experiment, increasing the amount of lime and sodium carbonate in the proportions indicated by the results.

If a decrease in the hardness is accompanied by an increase in alkalinity too much sodium carbonate has been added and the quantity used should be decreased in making a second experiment (see p. 48).

If the water has been softened down to between 4° and 6° of hardness without increasing the alkalinity a second experiment need not be made (see p. 50).

II. *To Soften with Caustic Soda and Lime.*—In London water the temporary hardness exceeds the permanent hardness, and if caustic soda is to be employed it should be used in conjunction with lime (see p. 49 (*c*)).

Calculate as shown above the number of grains of caustic soda and the number of grains of lime required. Convert grains to grams and weigh out the necessary quantities.

Mix the lime to a thin paste with water, add the caustic soda dissolved in a small quantity of water, mix with the 10

gallons of water to be softened and stir well. Allow to stand for several hours and then proceed as in I.

Water-Softening by the Permutite Process.

Another process for water-softening, known as the "*permutite process*," has recently been introduced.

Sodium permutite, artificial zeolite, is a hydrated silicate of sodium and aluminium formed by fusing together quartz (SiO_2), china clay ($Al_2O_3\ 2SiO_2\ .\ 2H_2O$), and sodium carbonate.

After extraction with water a crystalline mass, which may be represented by the formula $Na_2O\ .\ 2SiO_2Al_2O_3\ .\ 6H_2O$, is obtained.

When water containing calcium and magnesium salts is filtered through a considerable layer of this material (60-100 cm. in depth) the calcium and magnesium replace the sodium of the permutite and the water is thereby softened.

The reactions which take place may be represented thus:

$$\underset{\text{"Sodium permutite".}}{Na_2O\ .\ 2SiO_2\ .\ Al_2O_3} + CaCO_3 \rightarrow Na_2CO_3 + \underset{\text{"Calcium permutite".}}{CaO\ .\ 2SiO_2\ .\ Al_2O_3}$$

$$\underset{\text{"Sodium permutite".}}{Na_2O\ .\ 2SiO_2\ .\ Al_2O_3} + CaSO_4 \rightarrow Na_2SO_4 + \underset{\text{"Calcium permutite".}}{CaO\ .\ 2SiO_2\ .\ Al_2O_3}$$

The sodium permutite when exhausted can be regenerated by passing a concentrated solution of salt through the permutite layer, when the following reaction takes place:—

$$\underset{\text{"Calcium permutite".}}{CaO\ .\ 2SiO_2\ .\ Al_2O_3} + 2NaCl \rightarrow \underset{\text{"Sodium permutite".}}{Na_2O\ .\ 2SiO_2\ .\ Al_2O_3} + CaCl_2$$

It should be noted that in the case of water having temporary hardness the water will be left alkaline owing to the formation of sodium carbonate (see note, p. 47).

Chapter III.

SOAP.

Soaps as ordinarily understood are either the sodium salts (hard soaps) or potassium salts (soft soaps) of fatty acids of relatively high molecular weight.

Resins are also used in the manufacture of some soaps and contain an acid of high molecular weight known as abietic acid ($C_{44}H_{64}O_5$).

The raw materials from which soaps are manufactured vary considerably, but they are, with the exception of resin, animal or vegetable fats or oils.

Chemically, the fats and oils are composed of the glyceryl esters of the fatty acids, and the action of the caustic alkalis used to convert them into soaps consists in the production of the sodium or potassium salts of the fatty acids with the accompanying formation of glycerol.

This change may be regarded as an example of "*hydrolysis*," the term "*saponification*" is, however, more generally used to describe the special case of the hydrolysis of fats by alkalis in the production of soap.

Taking tristearin as a typical example of a glyceryl ester of a fatty acid, and caustic soda as the alkali used to effect saponification, the reaction may be represented as follows :—

$$\begin{array}{l} CH_2 \cdot OOC \cdot C_{17}H_{35} \\ | \\ CH \cdot OOC \cdot C_{17}H_{35} \\ | \\ CH_2 \cdot OOC \cdot C_{17}H_{35} \end{array} \quad \begin{array}{l} Na\,OH \\ \\ Na\,OH \\ \\ Na\,OH \end{array} \rightarrow \underset{\text{Sodium stearate.}}{3C_{17}H_{35}COONa} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Tristearin. Glycerol.

In the presence of a suitable catalyser fats can be split up by the action of steam, i.e. by hydrolysis, into fatty acid and glycerol.

$$\begin{array}{l} CH_2 . OOC . C_{17}H_{35} \\ | \\ CH \ . \ OOC . C_{17}H_{35} \\ | \\ CH_2 . OOC . C_{17}H_{35} \end{array} + 3HOH \rightarrow \underset{\text{Stearic acid.}}{3C_{17}H_{35}COOH} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Tristearin. Glycerol.

The fatty acid is separated from the aqueous solution of glycerine and converted into soap by neutralisation with sodium carbonate.

$$2C_{17}H_{35}COOH + Na_2CO_3 \rightarrow \underset{\substack{\text{Sodium stearate} \\ \text{(Soap).}}}{2C_{17}H_{35}COONa} + H_2O + CO_2$$

This method is chiefly employed where it is necessary to separate the glycerol completely, and also to use up the more liquid portions of the fatty acids obtained after the separation of the stearic and palmitic acids required for the manufacture of candles (see p. 258).

The fatty acids thus obtained are usually dark in colour and the soap prepared from them is generally considered to be inferior to that prepared by the saponification process.

The fats used in making soaps vary considerably in composition, but the following are given as examples, together with the names of the principal fatty acids contained in them, these acids being present in the form of their glyceryl esters :—

Fat or Oil.	*Acids.*
Tallow	Stearic, oleic, palmitic
Olive oil	Oleic, palmitic, linoleic
Palm oil	Palmitic, oleic (some of the palmitic acid may be present in the free state)
Cotton-seed oil	Oleic, linoleic, stearic, palmitic
Castor oil	Ricinoleic, stearic
Cocoa-nut oil Palm-nut oil	Myristic, lauric, palmitic, oleic.

The preparation of different types of soap on a large scale will be dealt with in the course of the lectures; soap may, however, be prepared on a small scale in the laboratory by the following methods :—

PREPARATION OF SOAP FROM FAT OR OIL.

I. BY SAPONIFICATION WITH CAUSTIC SODA.

Weigh out 10 gms. of fat or oil into a large porcelain dish and warm on a water bath.

Dissolve 1·5 gms. of caustic soda in about 25 c.c. of water, add to the warm fat or oil and stir well.

Continue the heating, stirring at intervals and adding more water, if necessary, until saponification is complete.

If the process is carefully carried out the mixture should become milky in appearance, with the production of a considerable amount of froth and lather on stirring. When this stage is reached some of the mixture should be removed from the dish and treated with hot *distilled* water in a test tube. If saponification is complete a clear soapy solution will be obtained, but if unsaponified fat is still present the solution will be turbid and the heating with sodium hydroxide must be continued.

When saponification is complete remove the dish from the water bath and allow the soap to stand until it forms a firm cake.

Some of the soap thus prepared may then be examined as described under Reactions of Soap (see below).

II. BY HYDROLYSIS TO FATTY ACID AND NEUTRALISATION WITH SODIUM CARBONATE.

The conversion of fat to fatty acid and glycerine can be effected in a variety of ways; most of the process employed involve the use of superheated steam, but in the *Twitchell Process* hydrolysis is effected by the action of steam under ordinary atmospheric pressure.

The reagent (Twitchell's reagent) required for this process is prepared by adding concentrated sulphuric acid to a mixture of oleic acid with an aromatic hydrocarbon, e.g. benzene or naphthalene, in such a manner that temperature during mixing does not rise above 30° C. The reaction which takes place in the case of benzene may be represented as follows:—

$$\underset{\text{Benzene.}}{C_6H_5}\boxed{.\,H + HO\,.}\underset{\text{Sulphuric acid.}}{SO_3H} \rightarrow \underset{\text{Benzene sulphonic acid.}}{C_6H_5SO_3H} + H_2O$$

$$\underset{\text{Benzene sulphonic acid.}}{HSO_3\,.\,C_6H_4H} + \underset{\text{Oleic acid.}}{C_{17}H_{33}COOH}$$

$$\rightarrow \underset{\text{Sulpho-benzene stearic acid.}}{C_6H_4\,.\,(SO_3H)\,.\,C_{17}H_{34}\,.\,COOH.}$$

The sulpho-benzene stearic acid separates out as a dark viscous oil, and when 0·5-1·0 per cent. of this substance is added to a fat (or oil), the fat can be hydrolysed to fatty acid and glycerine by passing steam (at atmospheric pressure) through the mixture for some hours.

On standing the fatty acids collect as an oily layer and the aqueous solution containing the glycerine is drawn off.

To convert the fatty acid to soap by neutralisation with sodium carbonate proceed in the following manner :—

Weigh out 10 gms. of the fatty acid into a large porcelain dish. Dissolve 2·5 gms. of sodium carbonate in about 20 c.c. water, add to the fatty acid, stir well and warm the mixture on a water bath until the evolution of carbon dioxide has ceased and a smooth homogeneous paste is obtained (see equation, p. 55).

To show that neutralisation is complete dissolve a portion of the mixture in hot distilled water. A clear soapy solution should be obtained. Free fatty acid will give rise to a turbid solution owing to its insolubility in water.

Some of the soap thus prepared may be examined as described below :—

REACTIONS OF SOAP.

I. Dissolve some of the soap in water, warm the solution and add a slight excess of dilute sulphuric acid. The solution becomes turbid, and on gently warming, a clear, oily layer (fatty acids) separates at the surface.

Taking sodium palmitate as an example of a soap the reaction may be represented by the equation :—

$$\underset{\text{Sodium palmitate (soluble in water).}}{2C_{15}H_{31}.COONa} + H_2SO_4 \rightarrow \underset{\text{Palmitic acid (insoluble in water).}}{2C_{15}H_{31}.COOH} + Na_2SO_4$$

II. Dissolve some of the soap in water and add saturated brine. A curdy precipitate of soap separates out.

Soap is soluble in water, but insoluble in the presence of excess of salt.

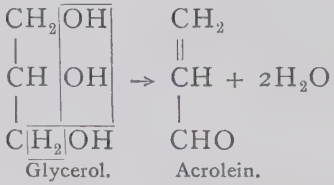
III. If soap is prepared by the saponification process as described in method I. above, the glycerol liberated by the saponification of the fat will be left in the soap * and its presence may be shown in the following way :—

* When soap is prepared on a large scale most of the glycerol is removed from the soap during the process of manufacture, and soap as a rule does not

Dissolve about 5-10 gms. of the soap in water (about 200 c.c.), warm the solution on a water bath and add a slight excess of dilute sulphuric acid. Continue to warm until the fatty acids have separated as a clear oily layer and the solution below is only slightly turbid.

Cool and remove the cake of fatty acids (see p. 61). Neutralise the solution by adding a slight excess of barium carbonate, filter and concentrate the filtrate to a small bulk (i.e. to the consistency of a syrup). Add to a portion of the residue about twice its weight of potassium acid sulphate and heat strongly. The glycerol is thereby converted into acrolein (C_3H_4O), which may be recognised by its extremely penetrating odour resembling that of burning fat.

The potassium acid sulphate acts as a dehydrating agent, with the result that two molecules of water are removed from the glycerol thus :—



Glycerol. Acrolein.

The presence of glycerol may also be shown by mixing another portion of the residue with a saturated solution of borax to which sufficient phenolphthalein has been added to produce a distinct red colour. The red colour is discharged, but returns again on boiling.

This is due to the action of glycerol in preventing the hydrolysis of the borate (see p. 40). On boiling, hydrolysis takes place with the consequent return of the red colour.

COMMERCIAL SOAPS.

In order to suit various requirements, soaps in great variety have been placed upon the market, but by far the largest quantities of soap are used for laundry, toilet and other household purposes.

The properties and methods of preparation of the most common types of soap will be dealt with in the course of the

contain any appreciable amount of glycerol (see p. 68). Soap prepared by method II. should not contain any glycerol, since the aqueous solution containing the glycerol is separated from the fatty acids before the latter are neutralised.

lectures, and it is only necessary here to consider such properties of the soap as must be taken into consideration in making an examination of a commercial soap.

Lewkowitsch* considered that *pure* commercial soaps, made on a large scale, should contain 30 per cent. of water and 60-64 per cent. of combined fatty acids, and that such soaps might be described as "*genuine soaps*".

Soaps containing less than 30 per cent. of water have either become dried on exposure to the air or have been artificially dried.

The substances obtained by the action of alkalis on resins, which consist chiefly of the sodium salt of abietic acid (see p. 54), are hardly to be described as soaps, but the substitution of resin for part of the fatty matter used in making soap is considered to be legitimate. The introduction of resin is, however, disadvantageous in the case of soaps used for laundry work, since white goods, if washed repeatedly with resin soaps, become a bad colour, i.e. develop a yellowish-brown tinge.†

In addition to "genuine soap" commercial soaps may contain a slight excess of free alkali; this is more particularly the case with genuine "mottled soaps".

Lower quality soaps are often "*filled*" or adulterated with substances such as sodium carbonate, sodium silicate, borax and occasionally also with other mineral matter, chalk, grit, etc. These substances are added with a view to "hardening" the soap, i.e. their presence makes it possible to increase the water content of the soap without making it unduly soft.

Soft Soaps consist of a mixture of the potassium salts of the fatty acids with a solution containing all the glycerine from the fat, together with a slight excess of caustic potash and potassium carbonate.

Toilet Soaps are as a rule "*milled*" soaps. "Milled" soaps are prepared by carefully drying shavings of the soap so that they lose about 20 per cent. of water. The soap is then crushed or "milled" and finally compressed to form a firm cake.

A soap prepared in this way will usually contain about 80 per cent. of combined fatty acids.

Cereal Soaps are prepared by treating starchy and albuminous materials, such as are found in the germ and bran of

* "Technology and Analysis of Oils, Fats and Waxes," Vol. III.

† See Jackson, "Detergents and Bleaching Agents Used in Laundry Work". Cantor Lectures, Royal Society of Arts, 1907.

various cereals, e.g. maize, oats etc., with a strong solution of caustic soda.

A considerable amount of alkali is taken up and the sodium salts of amino acids formed; these, it is claimed, have detergent properties similar to those of the sodium salts of the fatty acids, i.e. to soap. Further, it is claimed that these detergent properties are unaffected by the presence of salts of lime or magnesia, or of common salt, in the water. To neutralise the excess of alkali used during the process of manufacture, a suitable proportion of free fatty acid may be subsequently added, and cereal soaps will thus usually be found to contain some real soap.

Difficulty will probably be experienced in trying to separate the fatty acid from such soaps, since on the addition of hydrochloric acid (see p. 61) a curdy mass separates which contains the residue of the cereal matter used, as well as the fatty acid. The fatty acid may, however, be separated, after acidification, by extraction with ether (see p. 73).

THE CHEMICAL EXAMINATION OF SOAPS.

In making an examination and valuation of a commercial soap it is hardly necessary to make a complete chemical analysis embracing a search for all substances that may possibly be present, and such a course would be of little practical use.

The foregoing remarks on commercial soaps show that the most important factors to be taken into consideration in the examination of a soap are :—

I. Determination of the Amount of Fatty Acids, since this gives a measure of the amount of genuine soap present. *The detection of resin* in the fatty acids is also of importance if the soap is to be used for laundry work (see p. 59).

II. Determination of Alkali, Combined, Free Caustic Alkali and Alkaline Salts.—The amount of combined alkali, i.e. alkali present combined with the fatty acids to form soap, should be determined, and also the quantity and nature of the free alkali * (if any).

* *Free alkali.*—The term "free alkali" includes all substances other than soap which have an alkaline reaction, i.e. caustic alkali, and salts such as sodium carbonate, carbonate, silicate, etc., which are referred to as "alkaline salts".

Any *insoluble mineral matter* can be conveniently determined after the removal of free caustic alkali and alkaline salts (see p. 67).

III. Determination of Water in Soap.—The results of I. and II. will, as a rule, give a sufficiently accurate measure of the actual amounts of soap and alkali present (see p. 66), and it is by no means always necessary to make a direct determination of the water present in the soap, though in some cases it may be advisable to do so.

IV. Examination for Other Substances Occurring in Soap.—Glycerol, unsaponifiable matter, etc.

METHODS OF SOAP ANALYSIS.

Sampling.—In order to avoid serious errors care must be taken in sampling the soap, especially for the determination of water. On exposure to the air soap dries on the surface and a coating or "skin" is formed on the outside, which to some extent protects the inner portions from loss of water by evaporation.

The sample for analysis should therefore be taken from the centre of the bar or cake in the case of a hard soap, and from the centre of the mixture in the case of a soft soap.

Determination of Fatty Acids.

Dissolve 5-10 gms. of soap, weighed accurately to two places of decimals, in about 250 c.c. of distilled water, warm the solution, add a few drops of methyl orange and then dilute hydrochloric acid until there is a slight excess of acid present.

Dilute sulphuric acid may also be used, but if traces are left in the fatty acids it is liable to produce charring during the subsequent process of drying.

If glycerol is to be tested for sulphuric acid should be used, as any excess of acid can then be removed as barium sulphate (see p. 58).

Heat on a water bath until the fatty acids separate out as a clear oily layer and the liquid below is only slightly turbid. This operation should be carried out in a tall narrow beaker, so that the fatty acid separates as a fairly thick, compact layer. Cool and remove carefully the solidified cake of fatty acids with a spatula, rinse with cold water and place on a filter

paper. Carefully scrape off any small particles of fatty acids adhering to the sides of the beaker and add to the cake.

Dry the cake by touching lightly with a filter paper, transfer to a weighed dish and melt by heating in the steam oven for a few minutes.

If the melted fatty acids are observed to be free from moisture, they should be cooled in a desiccator and weighed. If, however, drops of water are observed on melting the cake, the fatty acids should be allowed to cool and the cake should again be dried with filter paper as described above.

From the weight of fatty acid thus obtained the percentage of fatty acids in the soap can be found.

Should the fatty acids be found to remain liquid or inconveniently pasty on cooling, this difficulty can be overcome by adding 5 gms. of shredded beeswax or paraffin wax to the mixture, and heating until the mixture of the fatty acids and wax has collected as a clear transparent layer. On cooling, the cake is removed, washed and dried as previously described. To obtain the weight of fatty acids the weight of added wax must be deducted from that of the cake.

Owing to the solubility of myristic and lauric acids in water, this method of determining the fatty acids will yield low results in the case of soaps made from palm-nut oil and cocoa-nut oil (see p. 55), and more accurate results can be obtained by bringing the fatty acids into ethereal solution (see p. 73).

Detection of Resin in Fatty Acids.

Dissolve a small portion of the dried fatty acids (about the size of a pea) in about 2 c.c. of acetic anhydride, in a dry test tube, heating gently if necessary. Cool the solution and add two or three drops of a *cold* mixture of equal volumes of glacial acetic acid and strong sulphuric acid.

If resin acids are present an unmistakable violet colour will be produced.* (This colour is fugitive, but if the solutions are well cooled it is very pronounced.)

It may be noted that soaps containing resin are often yellow in colour, such, for example, as many of the ordinary household soaps.

* The only substance other than resin likely to be met with in soap which will give a similar colour is cholesterol, from wool fat. This may be eliminated by shaking a solution of the soap, before decomposing with acid, with ether or petroleum ether, either of which will extract the cholesterol.

The presence of the resin tends to the production of a copious lather when the soap is dissolved in water.

Examination of Soap for Free Alkali (see note, p. 60).

Before making any determination of the alkali present in a soap it is advisable to examine the soap in order to ascertain whether any free alkali is present, and if so in what form.

Soap is soluble in alcohol whereas, with exception of caustic soda, the other alkaline substances which may be present in soap, e.g. sodium carbonate, sodium silicate, borax, are insoluble in alcohol.

A separation can therefore be made by treating some of the *dry* soap with absolute alcohol and heating on a water bath.

If soaps only or soaps and caustic soda are present the substance will dissolve completely in alcohol. The presence of caustic alkali may be shown by cooling the solutions and adding a few drops of phenolphthalein, the production of a pink colour shows the presence of caustic alkali.

It is essential that the soap should be moderately dry; if any considerable amount of water is present the alcohol will become diluted and some of the alkaline salts present, e.g. Na_2CO_3 etc., may dissolve.

The subsequent test for caustic soda is then of no value.

In the presence of water also the soap may hydrolyse to a slight extent (see below), and a pink colour will then be obtained with phenolphthalein even in the absence of caustic alkali.

It should be noted that a neutral soap dissolved in water will give a pink colour with phenolphthalein, but when dissolved in alcohol no pink colour is produced. This is explained by the fact that soap in the presence of water undergoes *hydrolysis* with the formation of a small amount of caustic soda, thus :—

$$\underset{\text{Sodium stearate.}}{C_{17}H_{35}COONa} + C_{17}H_{35}COO\boxed{Na + HO}H$$

$$\rightarrow \underset{\text{Acid sodium stearate.}}{C_{17}H_{35}COONa \,.\, C_{17}H_{35}COOH} + NaOH$$

The action of water may be demonstrated by dissolving a little dry soap in alcohol and adding a few drops of phenolphthalein. No colour or only a very faint colour will be produced. If the solution be then diluted with a considerable

volume of water the development of marked pink colour will be observed.

Sodium carbonate, silicate etc., together with any substances insoluble in water (if any) will be left as an insoluble residue when the soap is dissolved in alcohol.

This residue should be filtered off, washed with warm alcohol and then treated with hot water. The alkaline salts mentioned above will be dissolved and any matter insoluble in water can be removed by filtering.

The filtrate can then be examined for carbonate, silicate and borate in the usual manner (see p. 34).

The presence of carbonate will be readily detected by the action of hydrochloric acid, but since silicate and borate are often only present in relatively small quantities, it is found more convenient in actual practice to ash some of the soap and to examine the ash for these substances, rather than to attempt to identify them in the residue obtained after extracting with alcohol.

It is necessary to point out that before testing for the alkaline salts the soap must be removed, either by dissolving out in alcohol, or in the case of borate and silicate by ashing, since in the presence of soap or fatty acid some of the tests described on pages 34-36 are valueless.

Examination of Ash for Silicate and Borate.—Heat some of the soap in an iron spoon until all the organic matter has been destroyed and a well-charred residue is obtained. Extract with water, filter and test portions of the filtrate for borate and silicate as described on page 35.

The soap itself will yield carbonate on ignition, hence it is useless to test the ash for carbonate.

If there is any appreciable residue insoluble in water left after filtering off the alkaline salts, it should be examined under the microscope. Some form of grit etc. or small quantities of organic matter may be present.

Determination of Combined Alkali.

The combined alkali is usually obtained by determining the *total alkali* in the soap and also the *free alkali*, the *combined alkali* is then arrived at by difference.

Total Alkali.—The determination of the total alkali may be combined with the determination of the fatty acids (see

p. 61) by using an accurately measured volume of standard acids for decomposing the soap.

After the removal of the cake of fatty acids, the acid liquor is filtered to remove traces of fatty acid and the excess of acid is titrated back with standard alkali (seminormal).

The total alkali may, however, also be determined by dissolving 5 gms. of soap in water (about 250 c.c.) and titrating the solution with seminormal acid, using methyl orange as indicator, as the insoluble fatty acids liberated are without action on this indicator.

The alkali is calculated as Na_2O.

1 c.c. N/2 acid = 0·0155 gm. Na_2O.

If no free alkali is present, then

Total alkali = combined alkali.

Determination of Free Alkali, Caustic Alkali and Alkaline Salts.

The free alkali may be present as caustic alkali or alkaline salts or both.

Free Caustic Alkali.—5 gms. of the sample, after drying if necessary (see p. 63), are heated with absolute alcohol on a water bath in a flask *loosely* corked to prevent absorption of water from the air. The hot solution is filtered rapidly * through a filter previously washed with alcohol, and any insoluble residue is transferred to the filter and washed two or three times with hot alcohol. A few drops of phenolphthalein are added to the filtrate and washings and the whole titrated with decinormal acid.

(1 c.c. N/10 acid = 0·0031 gm. Na_2O = 0·0040 gm. NaOH.)

It should be noted that on keeping, any free caustic alkali in the soap will gradually be converted to carbonate by action of atmospheric carbon dioxide.

Alkaline Salts.—The residue obtained after extraction with alcohol is dissolved in water and titrated with decinormal acid, using methyl orange as indicator.

The alkalinity is calculated in terms of Na_2O and this

* *Precautions to be taken in filtering.*—Care must be taken in filtering that no soap jelly separates out in the filter. The glass funnel may be warmed previous to use, the solution should be kept nearly boiling throughout the operation and only small quantities transferred at a time to the filter. If these conditions are carefully observed a hot-water funnel can be dispensed with.

amount, together with any Na_2O present as free caustic alkali, is subtracted from the total alkali to obtain the combined alkali.

(1 c.c. N/10 acid = 0·0031 gm. Na_2O.)

If the free alkali is present entirely as carbonate, the percentage of Na_2CO_3 instead of Na_2O may be stated in the final results.

(1 c.c. N/10 acid = 0·0053 gm. sodium carbonate.)

The amounts of carbonate, borate and silicate in the above residue can if necessary be determined by the methods described on pages 39-45. As, however, they are usually present only in relatively small amounts, such determinations need not as a rule be made.

If an appreciable quantity of silicate is present the silica may be conveniently determined in the acid solution obtained after the removal of the fatty acids. This solution can be evaporated to dryness with excess of hydrochloric acid and the silica determined as described on page 40.

Percentage of Actual Soap.

In order to obtain the percentage of *actual* soap, the percentage of combined alkali should be added to the percentage of *fatty anhydrides.*

The fatty acids may be calculated to fatty anhydrides thus:—

Taking stearic acid as an example,

$$\begin{matrix} C_{17}H_{35}COO\boxed{H} \\ C_{17}H_{35}CO\boxed{OH} \end{matrix} \rightarrow \begin{matrix} C_{17}H_{35}CO \\ C_{17}H_{35}CO \end{matrix}\!\!>\!O \xrightarrow{Na_2O} 2C_{17}H_{35}COONa$$

Stearic acid. Stearic anhydride. Sodium stearate.

2×284 550

Thus 568 parts of stearic acid are equivalent to 550 parts of stearic anhydride.

Therefore 100 parts of stearic acid are equivalent to $\frac{550}{568} \times 100$

$= 96{\cdot}8$ parts of anhydride.

Similarly it may be shown that

100 parts palmitic acid are equivalent 96·48 parts of anhydride.
100 ,, oleic ,, ,, ,, 96·8 ,, ,, ,,

If therefore the percentage of fatty acid is multiplied by 0·9675 and the result taken as fatty anhydride no serious error will be introduced.

Determination of Insoluble Mineral Matter in Soap.

Any insoluble mineral matter present will be left as a residue after the removal of soap and caustic alkali by alcohol, and the alkali salts by water.

This residue should be ignited to remove any organic matter and weighed.

Determination of Water in Soap.

Five gms. of soap, in the form of fine shavings, are heated in a porcelain dish large enough to allow of the soap being stirred freely with a glass rod, which has previously been weighed with the dish.

The heating is carried out in a steam oven and is continued until the soap has attained a constant weight.

Any volatile substances present in the soap, e.g. ethereal oils used for scenting etc., will be lost during drying and returned as moisture.

Soaps bought in the ordinary way will, before reaching the laboratory, have lost more or less of the water they originally contained, the extent of the loss depending both on the nature of the soap, the time and the conditions under which it has been kept.

If the soap contains a considerable proportion of caustic soda part of the loss on drying will be compensated for by the absorption of carbon dioxide.

For these reasons the direct determination of water in soaps does not afford a very reliable means of valuation.

OTHER SUBSTANCES OCCURRING IN SOAPS.

In addition to the substances already dealt with, soaps may contain a variety of other substances, of which the most important are glycerine, unsaponified or "neutral" fat, free fatty acid, unsaponifiable matter,* and phenols.

* *Unsaponified or neutral fat* is fat which has not been converted into soap.
Unsaponifiable matter is organic matter other than fat, e.g. mineral oils, etc., and which therefore cannot be converted into soap.
Free fatty acids are seldom found in soap though, as already noted (see p. 63), *acid soaps* are formed when soap is dissolved in water. If free fatty acid

I. *Glycerine.*—Small quantities of glycerine are occasionally found in ordinary hard soaps, and considerable quantities may be added to "milled" toilet soaps.

Soft soaps may contain practically all the glycerine formed during the process of saponification.

The method of detecting glycerine in soap has already been described under "Reactions of Soap" (see p. 57).

II. *Unsaponified or "Neutral Fat".*—Unsaponified fats or oils are very seldom met with in ordinary soaps, but in case of "super-fatted" soaps, the soap may be admixed with olive oil etc.

A soap containing unsaponified fat will not give a clear solution with hot distilled water, and a turbid solution after any insoluble matter, e.g. grit etc., has settled points to the presence of unsaponified fat or free fatty acid (possibly also unsaponifiable matter, see below).

The unsaponified fat may be separated by shaking the aqueous solution with ether, any free fatty acid having first been neutralised with a little caustic soda. The ethereal layer is separated and the ether distilled off on a water bath, the residue will contain the unsaponified fat (possibly also unsaponifiable matter, see below).

III. *Unsaponifiable Matter.*—Small quantities of substances of the nature of mineral oils, e.g. paraffin oil, turpentine, etc., are sometimes added to soap with a view to increasing its cleansing powers.

These substances will be removed together with any unsaponified fat when the soap solution is extracted with ether (see above).

The residue obtained after the removal of the ether may be heated with a little alcoholic potash.

The *unsaponified fat* is thus converted into soap which goes into solution, and the *unsaponifiable matter* remains unchanged.

Since the unsaponifiable substances found in soap are usually volatile in steam they may often be readily detected by dissolving a considerable quantity of the soap, 50-100 gms., in water and distilling the solution in steam. Considerable frothing occurs under these conditions and it is therefore better,

is present an alcoholic solution of the soap will be acid to phenolphthalein. The amount of such free acid may be determined by titrating this solution with decinormal sodium hydroxide solution.

before distilling, to convert the soap into an insoluble barium soap by the addition of a slight excess of barium chloride

Any "oily" substance collected in the distillate should be carefully separated from the aqueous layer (by means of a separating funnel), dried over calcium chloride and, if present in sufficient quantity, redistilled.

If a known weight of soap was used for the experiment, the volume of liquid thus distilled will give an approximate measure of the quantity of unsaponifiable matter present.

More complete methods for determining the quantities of neutral fat and unsaponifiable matter are given in "Chemical Technology and Analysis of Oils and Fats," Lewkowitsch (Macmillan).

IV. *Carbolic Acid.*—Disinfecting soaps usually contain "carbolic acid" (a mixture of phenols and cresols), which may be recognised by its characteristic odour.

If present in sufficient quantity a determination of the amount can be made by the following method:—

Weigh out about 100 gms. of the soap, dissolve in hot water and add sufficient caustic soda to make the solution strongly alkaline. Then add common salt to "salt out" the soap (see p. 57), filter off the curdy soap and wash it with saturated brine. Concentrate the filtrate which contains the phenols and cresols as sodium phenoxides, and precipitate any soap still retained in the filtrate by the addition of more salt. Filter again, and concentrate the filtrate to a small bulk.

Transfer the solution to a stoppered graduated cylinder of 50 c.c. to 100 c.c. capacity, add sufficient salt so that some remains undissolved, and acidify with sulphuric acid. The volume of separated phenols is then read off and the number of c.c., multiplied by 1·05,* may be taken as the number of gms. present. If greater accuracy is required the separated "carbolic acid" should be extracted by ether, the ether distilled off on a water bath and the residue weighed.

Discussion of the Results of Soap Analysis.

In making any valuation of a soap the purpose for which the soap is sold must be taken into consideration.

A soap which is to be used for laundry work requires to be more carefully selected than a soap which is to be employed for ordinary household purposes, since the presence of

* See page 265.

substances such as free alkali, resin, etc., may produce injurious effects with delicate textile fabrics (see p. 59, also Chap. IV.).

Soap used for laundry work should be a neutral "genuine soap" (see p. 59), and should not contain: (1) grit or insoluble matter, (2) free alkali, either caustic or in the form of alkaline salts, (3) resin.

The action of soap and water as a detergent will be dealt with in the course of the lectures, but it should be noted here that the nature as well as the quantity of the fatty acids in a soap is of some considerable practical importance.

A list of the principal fatty acids met with in soaps together with their molecular weights is given below:—

Formula.	*Molecular Weight.*
Saturated Acids:—	
Lauric acid, $C_{11}H_{23}.COOH$	200
Myristic „ $C_{13}H_{27}.COOH$	228
Palmitic „ $C_{15}H_{31}.COOH$	256
Stearic „ $C_{17}H_{35}.COOH$	284
Unsaturated Acids:—	
Oleic acid, $C_{17}H_{33}.COOH$	282
Linoleic acid, $C_{17}H_{31}.COOH$	280
Ricinoleic acid, $C_{17}H_{32}OH.COOH$	298

Taking soaps made from fatty acids of the same series, experience shows that the soaps of acids of high molecular weight possess lathering * and cleansing properties superior to those of soaps made from acids lower in the series. If lauric acid (m.w. = 200) and palmitic acid (m.w. = 256) be taken as examples of fatty acids of the same series, then soaps containing a high percentage of sodium palmitate would be superior to those containing a high percentage of sodium laurate.

In making such comparisons the solubility of the soaps must be taken into account, and as a rule the solubility of a soap decreases as the molecular weight of the fatty acids increases, so that many soaps which are otherwise suitable for laundry work possess the disadvantage of not being readily soluble in cold water.

The soaps of oleic acid (m.w. = 282) are, however, among

* *Lathering power of soap.*—A good soap will produce a good lather, but lathering alone cannot be taken as proof of a good soap since substances such as sodium resinate produce a copious froth or lather (see p. 62).

the most soluble of all soaps, and these soaps therefore combine the advantages of high molecular weight and complete solubility in cold water.

It may, therefore, be stated that a good soap for laundry purposes should consist of the sodium or potassium salts of fatty acids of high molecular weight, a proportion of these acids being oleic acid, associated with water and practically nothing else.

THE NATURE OF THE FATTY ACIDS PRESENT IN A SOAP.

The separation, or even partial separation, of the fatty acids of a soap into the constituent fatty acids is an extremely complex matter and is not attempted in the practical examination of a soap as described above, but it may be noted that if a considerable proportion of oleic acid is present, the separated fatty acids will be of an oily consistency and will not set well on cooling.

Some indication of the nature of the fatty acids may also be obtained by a careful comparison of the amounts of combined alkali and fatty acid present, since the higher the mean molecular weight of the fatty acids, the lower will be the amount of combined alkali.

This may be shown by considering one or two typical examples.

If lauric acid be taken as an example of a fatty acid of relatively low molecular weight (200) and stearic acid as an example of a fatty acid of relatively high molecular weight (284) the percentage of Na_2O in their respective sodium salts can be calculated from the following equations :—

$$2C_{11}H_{23}COOH + Na_2O \rightarrow 2C_{11}H_{23}COONa + H_2O$$

Lauric acid.		Sodium laurate.
2 × 200	62	2 × 222
200	31	222

Therefore 222 parts of sodium laurate contain 31 parts Na_2O,

$$\text{or 100 parts of sodium laurate contain } \frac{31 \times 100}{222}$$

$$= \underline{14{\cdot}1 \text{ per cent. } Na_2O.}$$

$$2C_{17}H_{35}COOH + Na_2O = 2C_{17}H_{35}COONa + H_2O$$

Stearic acid.		Sodium stearate.
2 × 284	62	2 × 306
284	31	306

Therefore 306 parts sodium stearate contain 31 parts Na_2O,

or 100 „ „ „ „ $\frac{31 \times 100}{306}$

$= 10{\cdot}1$ parts Na_2O

$= 10{\cdot}1$ per cent Na_2O.

Similarly it may be shown that sodium oleate (oleic acid, m.w. = 280) and sodium myristate (myristic acid, m.w. = 228) contain 10·2 per cent. and 13·6 per cent. Na_2O respectively.

If, therefore, the amount of Na_2O present in 100 parts of *actual soap* (i.e. calculated by the addition of the amounts of fatty anhydrides and *combined* Na_2O, see p. 66) approximates to 10-11 parts, it may be assumed that acids of relatively high molecular weight are present, whereas if the amount of Na_2O approximates to 13-14 parts, acids of relatively low molecular weight are present.

In making an examination of a soap the results will usually be obtained in terms of fatty acid and combined alkali, and instead of calculating the amount of Na_2O present in 100 parts of actual soap, the same information as to the nature of the fatty acids may be deduced by considering the ratio of combined Na_2O to fatty acid.

The equations given above show that—

In the case of sodium laurate $\frac{\text{Fatty Acid}}{\text{Combined } Na_2O} = \frac{200}{31} = 6{\cdot}45.$

„ „ „ stearate „ „ $= \frac{284}{31} = 9{\cdot}11.$

Similarly it may be shown that this ratio gives 9·0 in the case of sodium oleate and 7·3 in the case of sodium myristate.

Thus if the figure obtained on dividing the percentage of fatty acid in the soap by the percentage of combined alkali approximate to 9·0, the mean molecular weight of the fatty acids is high, and if it approximates to 7·0 the mean molecular weight is low.

If the above considerations indicate the presence of acids of relatively low molecular weight, it is probable that the soap was made from a mixture containing considerable proportions of palm-nut oil or cocoa-nut oil (see table, p. 55). In this case a more accurate determination of the mean molecular weight of the fatty acids should be made.

Determination of the Mean Molecular Weight of the Fatty Acids.

The mean molecular of the fatty acids may be determined by dissolving 2·5 gms. of the separated fatty acids (see p. 61) in alcohol and titrating the solution with a seminormal solution of sodium hydroxide.

For this determination it is essential that the fatty acids should previously have been well washed with water to remove mineral acid, and then carefully dried.

Since in the case of cocoa-nut oil and palm-nut oil some of the fatty acids present are soluble in water, a more accurate result is obtained, both for the determination of fatty acid and of the mean molecular weight, by decomposing the soap under ether and so bringing all the fatty acids into ethereal solution.

If this alternative method is adopted, dissolve 5 gms. of the soap in hot water, transfer to a separating funnel and decompose with hydrochloric acid. After cooling shake the solution with ether or petroleum ether (boiling-point below 80° C.) and allow to stand until the mixture has separated into two clear layers.

Separate the ethereal layer, shake the aqueous layer again with ether, and again separate the ethereal layer.

Distil off the ether and weigh the residue; this gives the weight of fatty acids and from this the percentage of fatty acids in the soap can be obtained (see p. 62). Dissolve the fatty acids in alcohol, add a few drops of phenolphthalein, and titrate the solution with a seminormal solution of sodium hydroxide.

From the amount of sodium hydroxide required to neutralise the fatty acid, calculate the weight of fatty acid which would be neutralised by 40 gms. of caustic soda. This gives the *mean equivalent* of the fatty acids, and since the acids present may be assumed to be monobasic, this is equal to their *mean molecular weight.*

If the mean molecular weight approximates to 280, acids of relatively high molecular weight are present, and if it approximates to 200, acids of relatively low molecular weight are present (see table, p. 70).

OTHER PREPARATIONS CONTAINING SOAP.

Dry Soaps, Soap Powders and Soap Extracts.

Dry Soaps are sometimes obtained in a shredded and sometimes in a powdered form.

Shredded Soaps are usually of the nature of desiccated soaps, i.e. soaps which are artificially dried and therefore contain a high percentage of fatty acid, usually about 80 per cent. They should be examined by the methods described above.

Soap Powders may contain dry soap only, but more often the dry soap is mixed with sodium carbonate or some other form of alkali. The amounts of fatty acid, free and combined alkali can be determined as described above, but as the soap is sometimes only present in relatively small quantities, and the proportion of alkaline salts may be large, the method should be modified in the following respects :—

For the determination of the fatty acid not less than 10 gms. of the powder should be used (see p. 61).

The residue, after the removal of the soap with alcohol, should be dissolved in water, the volume made up to 250 c.c. and 50 c.c. of the solution titrated with N/2 acid (see p. 65).

In the absence of free caustic alkali, the following alternative method may be employed and is specially suitable for powders containing only a small proportion of soap.

Five gms. of the powder are treated with absolute alcohol to dissolve out the soap. The residue is filtered off and washed several times with hot alcohol.

The alcoholic filtrate and washings are evaporated in a weighed dish on a water bath until all the alcohol is removed. After cooling the residue of soap is weighed.

If the result is required in terms of fatty acid, it may be assumed that 88 parts of fatty acids are obtained from 100 parts of anhydrous soap (see p. 71).

The residue insoluble in alcohol is dissolved in hot water and the alkali determined as described above. The powder should also be examined qualitatively for carbonate, borate and silicate (see p. 64), and if described as having bleaching properties, perborate should also be tested for (see p. 149).

Scourers, Household Cleansers, etc.

Numerous scourers and household cleansers are now being sold. These preparations usually contain a considerable

amount of grit mixed with alkali in some cases, and alkali and soap in others.

The presence of soap may be shown by heating the substance with hot water, filtering off the insoluble matter and adding hydrochloric acid to the filtrate. If soap is present an oily layer of fatty acid will be obtained on warming.

The amount of grit, soap and alkali present may be determined in the following manner :—

Five gms. of the dry powder are treated with absolute alcohol and the soap determined as described above.

The residue is treated with hot water, the solution is filtered and the alkali in the filtrate determined as above.

The insoluble matter is dried, ignited and weighed (see p. 67).

Some of the insoluble matter may be examined under the microscope and the size of the particles compared with those of the more common forms of grit, e.g. bathbrick, powdered pumice, fine sand, etc.

Soap Pastes, Stain-removers, etc.

Preparations consisting of a paste of soap and water, with or without the addition of some oxidising agent, e.g. sodium perborate, are sometimes sold as "stain-removers" or "grease extractors". A measure of the amount of soap in such preparations may be obtained from a determination of the fatty acid.

The presence of oxidising agent may be shown by means of the reactions described under Bleaching Agents, Chapter V.

Dry Cleaning Soaps.

See Chapter VI.

Metal Polishes, Furniture Polishes, etc.

These may contain soap, for methods of examination (see Chap. X.).

** Experiments on the Detergent Action of Soap Solutions.

The theoretical explanation of the detergent action of soap solutions will be dealt with in the course of the lectures, and

the following experiments are designed to demonstrate some of the more important factors which have to be taken into account in dealing with soap and water as a detergent for laundry purposes.

THE EMULSIFICATION OF GREASE OIL, ETC., BY ALKALINE SOLUTIONS.

When a mixture of oil and water is well shaken, the oil is distributed throughout the water in the form of fine particles or drops, but on standing the mixture rapidly separates into two layers.

If an alkaline solution is used instead of water, the oil remains distributed throughout the solution in the form of a fine suspension, producing a milky fluid or *emulsion.*

Mineral oils which are free from saponifiable matter cannot be readily emulsified by alkaline solutions, but in the presence of small amounts of saponifiable matter, a considerable amount of mineral oil can be held in a state of emulsification by an alkaline solution.

Thus the emulsifying action of an alkaline solution appears to be partly dependent on the presence of some saponifiable matter; this may be illustrated by the following experiments :—

Take four stoppered bottles (50-100 c.c. capacity) and number 1 to 4.

Into (1) and (2) introduce 5 drops of olive oil.
„ (3) „ 5 „ „ paraffin oil.
„ (4) „ 4 „ „ „ „ and 1 drop of olive oil.

To (1) add 25 c.c. of water and to each of the others add 25 c.c. of a 1 per cent. solution of sodium carbonate. Shake each bottle well and observe that in (1) and (3) the mixture rapidly separates into two layers, whereas in (2) and (4) an emulsion is obtained.

Soap dissolves in water giving a solution which is alkaline in reaction owing to the liberation of free alkali by hydrolysis (see p. 63).

The alkali thus liberated will by its emulsifying action assist the removal of dirt particles which contain saponifiable matter, e.g. grease, etc., but it must be emphasised that this is only one of the factors which have to be taken into con-

sideration in dealing with the detergent action of soap solutions.

THE "SURFACE-ACTIVITY" OF SOAP SOLUTIONS.

Allow a drop of water and also a drop of aqueous soap solution to fall on to a piece of woollen fabric; observe that the water maintains its spherical shape for a considerable time and is only slowly absorbed by the fabric, whereas the soap solution forms a flatter drop, spreads and is rapidly absorbed by the fabric.

By dissolving soap in the water the surface tension between the water and the fabric is lowered, the solution spreads over and wets the surface more readily than water, thus facilitating the cleansing of the fabric.

Substances which have this power of lowering the surface tension of the solvent in which they are dissolved are said to be "*surface-active*".

A measure of this "surface-activity" may be obtained by means of an instrument known as a *stalagmometer* (or "drop-measurer").

By means of this instrument the size of the drops, formed when an unsaponifiable oil is allowed to issue from a small orifice into a soap solution, can be compared with the size of the drops formed when the oil issues into water.

FIG. 5.

The Stalagmometer.—The stalagmometer consists of a pipette the lower end of which is bent through 180° (see Fig. 5). Near the other end is a small bulb. To the upper end of the instrument is attached, by means of a short piece of rubber tubing, a glass tube drawn out to a fine capillary. The lower end of the instrument is drawn out to a point and is then ground flat.

Attention to cleanliness and a little practice in manipulation are sufficient to ensure correct drop-formation.

The instrument is filled with oil to a point above the upper mark on the stem, and the lower end is dipped into the solution to be tested. Owing to air friction in the capillary, the oil issues slowly from the lower end of the stalagmometer into

the solution in drops, the size of which depends upon the tension of the interface separating the oil from the solution. A measure of the size of the drops is obtained by counting the number of drops formed while the liquid falls between the upper and lower marks on the stem of the instrument.

If the drops are allowed to form in pure water, they are large and the "drop-number" is small.

This is due to the large surface tension between the oil and the water, which does not allow the drop to be detached till it is very large and the force due to buoyancy correspondingly great.

The addition to the water of substances which lower the surface tension causes a diminution in the size of the drops and an increase therefore in the drop-number. Most substances exhibit only a small effect, but in the case of ordinary soaps the effect is very considerable.

Method of Using the Stalagmometer.

To Fill the Stalagmometer with oil, e.g. benzene, immerse the lower end of the instrument in a beaker containing this substance. Remove the capillary, attach the upper end of the instrument to a water pump and draw up the benzene until it stands well above the upper mark on the stem. Close the rubber tubing with a good pinch or screw clip and attach the capillary tube. The instrument is now ready for use.

To Compare the Drop-Number in Water with the Drop-Number in Soap Solution.—Fix the instrument in position with a clamp, release the clip and immerse the lower end of the instrument in a beaker containing water, so that the orifice is about an inch below the level of the water. When the benzene reaches the upper of the two marks start to count the drops and continue counting until the benzene falls to the lower mark and record the drop-number. Repeat the experiment and take the mean of the two results.

Fill the instrument again and this time immerse it to the same depth in an aqueous soap solution (0·5-1 per cent.). Count as before the number of drops formed by the benzene between the two marks on the stem. Take the mean of the results of two experiments.

It will be observed that the drops formed in the soap solution are considerably smaller than those formed in the water, and that in consequence the drop-number in the former case is greater than that in the latter.

The results obtained in a typical experiment were as follows:—

Drop-number in water, 28.
„ „ „ soap solution 195.

This experiment shows that when an oily surface is in contact with a soap solution, there will be a tendency owing to the "surface-activity" of the soap, for the oil to distribute itself in small drops, thus promoting the formation of an emulsion.

This effect, it should be noted, cannot be attributed to the action of the alkali liberated by hydrolysis, since it was shown in the experiment described on page 76, that the emulsifying action of alkali was dependent on the presence of saponifiable matter, whereas in the experiment just described the emulsifying effect is exhibited in the case of a neutral oil which is free from saponifiable matter.

COMPARISON OF THE DETERGENT ACTION OF VARIOUS SOAP SOLUTIONS.

A comparison of the cleansing powers of different solutions may be obtained in a direct and practical manner by washing pieces of dirty material in the solutions, under as nearly as possible the same conditions, and observing in each case the extent to which the dirt is removed.

It is obvious that this method can only yield reliable results if the material used is uniformly dirty, and owing to difficulty of obtaining such material in actual practice, it has been found advisable to use an artificially soiled material, obtained by coating a piece of fabric with a fine deposit of lampblack. This material can be conveniently prepared in the following manner:—

Preparation of "Dirty" Material.

Cut some white cotton fabric, which has been previously washed to remove the dressing and then well dried, into strips about 4 inches wide and about 20-25 inches long.

Shake up some finely divided lampblack in a considerable volume of benzene and pour some of the mixture into a flat-bottomed dish (a half-plate developing dish does very well for this purpose), pass each strip of cotton two or three times through the benzene, in a manner similar to that employed in developing a roll film.

The material should be kept as flat as possible during this operation, as if allowed to crease the deposit will not be uniform.

Suspend the strip, stretched flat, over a dish or sink until quite dry.

The material will be found to be fairly uniformly coated with lampblack.

The deposit at the ends of the strip will probably be less uniform than that covering the rest of the strip, but it should be found possible to cut off pieces of material 3-4 inches square on which the lampblack is evenly distributed.

If several strips are to be coated, the benzene and lampblack mixture in the dish should be renewed at frequent intervals and should be well shaken before pouring into the dish.

With a little practice in manipulation this method will be found to give satisfactory results.

Comparison of the Action of Aqueous and Alcoholic Soap Solutions on the "Dirty" Material.

Take two pieces of the "dirty" material (prepared as above) of the same size and shape (about 3-4 inches square) and immerse one in 200 c.c. of a 0·5 per cent. solution of soap in water, and the other in a 0·5 per cent. solution of the same soap in alcohol.

Heat the solutions on water bath for about 15 minutes, stirring at intervals. Remove the pieces of material from the solution and hang up to dry.

The aqueous soap solution will be found to have removed the dirt much more completely than the alcoholic solution.

Examination of the Soap Solutions.—Set aside some of the soap solutions used in the experiment which contain the dirt particles removed from the fabric during the washing process.

Observe that in the alcoholic soap solution the dirt particles rapidly settle to the bottom, leaving the soap solution nearly clear.

In the case of the aqueous soap solution this separation is only partial, most of the dirt remains suspended in the soap solution and may not settle for several days.

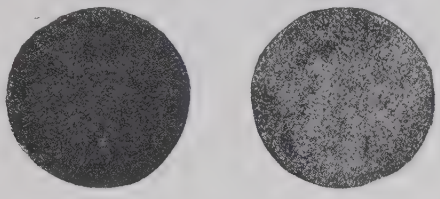
The greater cleansing action of the aqueous soap solution would, therefore, seem to depend on the fact that in this solution the dirt particles are in a more perfect state of suspension than in the alcoholic solution, and are thus removed more completely from the fabric.

In further illustration of this point the following experiment should be made:—

Shake up a small quantity of lampblack (about 0·1 gm.) with 100 c.c. of the alcoholic soap solution and warm the mixture on a water bath for about ten minutes. Stir well and filter through a disc filter, using a water pump.

Do the same experiment with the aqueous soap solution, using the same quantity of lampblack and the same volume of solution.

The alcoholic solution will be found to filter clear, or almost clear, and the lampblack will be left almost entirely on the filter paper, forming a thick black deposit.



A *B*

FIG. 6.—Residues obtained on filtering *A* alcoholic, *B* aqueous soap solutions of the same concentration containing equal weights of lampblack.

With the aqueous solution the filtrate is dark in colour, showing that some of the lampblack is still in suspension, and although some of the lampblack is left on the filter, the deposit is much less than that obtained from the alcoholic solution.

Thus in the case of the alcoholic soap solution the particles can be separated from the solution almost completely by filtration, whereas in the aqueous solution they are in a more perfect state of suspension and cannot be readily separated by this means.

A photograph of the deposits obtained on filtering 100 c.c. of a 0·5 per cent. aqueous and a 0·5 per cent. alcoholic soap solution containing 0·1 gm. of suspended lampblack is shown in Fig. 6.

TO SHOW HOW THE CLEANSING ACTION OF A SOAP SOLUTION VARIES WITH THE CONCENTRATION.

If the washing of fabrics is to be carried out without undue wastage of soap, it is important to know how far the cleansing action of a soap solution depends on the amount of soap present.

The following experiments are designed to show how some idea of the optimum concentration of soap for washing purposes may be obtained.

It is, however, important to remember that this concentration will vary with the nature and state of dryness of the soap used and also with the nature of the water, since with hard water more soap will necessarily be required than with soft water.

If pieces of uniformily dirty material of the same size and shape are washed in equal volumes of soap solutions of varying concentration, under exactly similar conditions, it should be possible, by carefully comparing the strips, to see with which concentration the dirt is most completely removed.

To do this it is first of all necessary to prepare a series of soap solutions of different concentrations.

If the maximum concentration used is 2 per cent., and 200 c.c. of solution are used for each experiment, these solutions can conveniently be prepared in the following manner:—

Dissolve 10 gms. of good, moderately dry, laundry soap in water and make up the volume to 500 c.c.

Take five beakers (300-350 c.c.), preferably of the same shape, and measure out the soap solution into them in the following manner:—

(1) 200 c.c. of prepared soap solution (concentration = 2 per cent.).
(2) 100 c.c. of prepared soap solution + 100 c.c. water (concentration = 1 per cent.).
(3) 50 c.c. of prepared soap solution + 150 c.c. water (concentration = 0·5 per cent.).
(4) 25 c.c. of prepared soap solution + 175 c.c. water (concentration = 0·25 per cent.).
(5) 12·5 c.c. of prepared soap solution + 187·5 c.c. water (concentration = 0·125 per cent.).

Cut five pieces of dirty material (3-4 inches square). These strips should all be of the same size and shape, and in selecting them care should be taken to see that the deposit is evenly distributed and of about the same depth in each case.

Immerse one piece of material in each beaker. Place the beakers on a hot plate or sand bath and heat until the soap solution boils.

The contents of each beaker should be stirred at intervals, each solution receiving as nearly as possible the same treatment. It may also be necessary to interchange the position of the beakers from time to time to ensure uniform heating.

Allow the solutions to boil for about 10 minutes. Remove the pieces of fabric from the solutions and put the solutions aside for further observation.

Rinse each piece of material twice with cold water, using about 200 c.c. of water for each rinsing, and spread out to dry.

Avoid squeezing or a streaked appearance may be obtained.

When the pieces of fabric are dry their appearances should be carefully compared.

The cleansing action, it will be noted, appears to be greatest with the intermediate concentrations of soap. The best results are usually obtained either with 0·5 or 0·25 per cent. of soap, whilst the 2 per cent. solution is often inferior in its cleansing action to the solution containing only 0·125 per cent.

These results are borne out by observations on the soap solutions used in the experiment, since on allowing these to stand for some time, it will be noted that the dirt particles separate out most slowly from the solution in which the cleansing action appeared to be the greatest.

The 2 per cent. and probably the 1 per cent. solution will form a jelly on cooling, thus preventing the further separation of the dirt particles; but as a rule considerable separation will take place in these solutions before they set.

If hand washers or washing machines are available, these experiments may be repeated on a larger scale, subjecting each piece of material to as nearly as possible the same treatment for the same length of time.

Such experiments should yield results similar to those obtained on the small scale.

As in the case of aqueous and alcoholic soap solutions, this relation between cleansing and suspending power may be further demonstrated by warming equal weights of lampblack with equal volumes of the different soap solutions and filtering through a disc filter.

It will be observed that the deposit left on the filter is least with the concentrations which were noted to have the best cleansing action.

Instead of making a fresh experiment, equal volumes of the dirty solutions obtained in the first experiment may be filtered, but this does not give strictly comparable results, since the solutions which have the best cleansing action will have removed more dirt from the fabric than the others and will therefore contain more dirt in suspension.

A photograph of strips of dirty material after washing

in 2 per cent., 0·25 per cent. and 0·125 per cent. soap solution respectively are shown in Fig. 7, together with the deposit obtained on filtering equal volumes of solutions of these concentrations, containing equal weights of lampblack.

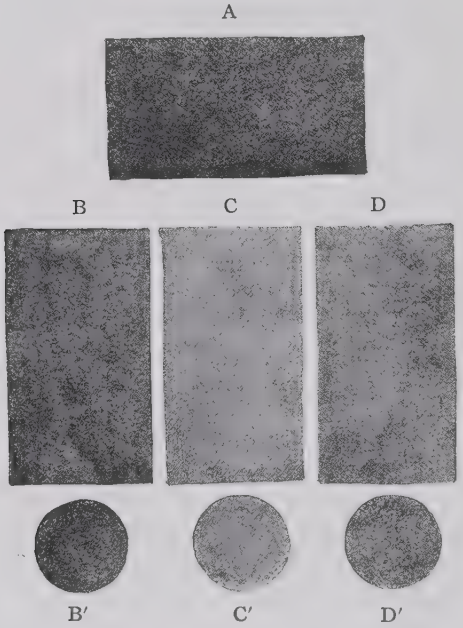


Fig. 7.—A, "dirty" material before washing; B, C, D, "dirty" material after washing B in 2 per cent., C in 0·25 per cent., D in 0·125 per cent. soap solution; B′, C′, D′, residues obtaining on filtering, B′ 2 per cent., C′ 0·25 per cent., D′ 0·125 per cent. soap solutions containing equal weights of lampblack.

If time allows, this method of experimenting may be extended to deal with a number of other problems in connection with the use of soap and water as a detergent.

The following subjects are suggested as being suitable for treatment in this manner:—

Comparison of the Detergent Action of Different Types of Soap, e.g. soaps made from fatty acids of relatively high and relatively low molecular weight and from saturated and unsaturated acids.

In making such experiments it is advisable, unless pure soaps are available, to work with solutions containing equal weights of combined Na_2O, as in this manner any difference

in the water content of the soap is allowed for and a fair comparison is obtained.

Concentration of Soap Solution Required for Washing at Low Temperatures.—Most articles dealt with in the laundry are washed with boiling water, but woollen or silk goods are usually washed in lukewarm water (about 40° C.) The optimum concentration of soap required for washing at the latter temperature may be investigated in the manner previously described, by keeping the solutions for some time at 40° C. instead of raising them to the boiling point.

Comparison of the Cleansing Action of Soap Solutions with that of Other Detergents.—The detergent action of other substances commonly added to, or substituted for soap, e.g. alkaline resinates, bran water, cereal soaps, etc., may be investigated by this method, their action in each case being compared with that of an ordinary soap solution when used under exactly the same conditions.

EXPERIMENTS TO SHOW THAT SOAP IS TAKEN UP OR "ADSORBED" BY THE DIRT PARTICLES AND BY THE FABRIC DURING THE PROCESS OF WASHING.

It is a matter of common observation in laundry work that the introduction of a considerable bulk of dirty material into a lather of soap and water causes a rapid disappearance of the lather.

This disappearance of the lather may be partly accounted for by the taking up or "adsorption" of soap both by the dirt and by the fabric.

To demonstrate this the following experiments may be made:—

Make up a 0·5 per cent. solution of a good laundry soap.

Measure out 100 c.c. of distilled water into a stoppered bottle (capacity = 250 c.c.), and by running in the soap solution from a burette find the number of c.c. of soap solution required to produce a permanent (3 minutes) lather (usually about 2 c.c.).

(*a*) Take about 0·2 gm. of finely divided lampblack, wash it into a stoppered bottle with distilled water, adding in all 100 c.c. of water. Shake well. Run in soap solution as before until a permanent lather is obtained. It will be found that a greater volume of soap solution is required than with water alone.

(*b*) Introduce a piece of cotton wool (about 0·2 gm.) into a stoppered bottle, add 100 c.c. water, shake well, and again

determine the volume of soap solution required to produce a permanent lather. As in the previous experiment this will be found to be greater than that required by water alone.

This experiment may be repeated, using wool fibres instead of cotton wool. A similar result is obtained.

In carrying out these experiments the three minutes' limit for the lather should be strictly adhered to, since in the presence of the lampblack or cotton a copious lather, which at first appears quite permanent, will be often found to have disappeared within the prescribed three minutes.

Chapter IV.

TEXTILE FIBRES.

The fibres used in the manufacture of textiles fall naturally into three groups according to their origin :—

(1) Animal fibres.
(2) Vegetable ,,
(3) Mineral ,,

I. Animal Fibres.—Of these the most important are :—

Wool—hair fibre of the sheep.

Silk—from the mulberry silk worm (*Bombyx mori*), cultivated for that purpose.

Wild Silks, e.g. Tussah—from the larvæ of other moths not usually cultivated.

II. Vegetable Fibres.—Of these the most important are :—

Cotton—seed hairs of various species of *Gossypium.*

Bast Fibres—from stems of dicotyledonous plants, e.g. flax, hemp, ramie, jute.

III. Mineral Fibres.—Apart from fine threads of metal, glass, etc., used for embroidery, the only important representative of this group is *Asbestos* which consists chiefly of calcium and magnesium silicates.

Reactions of Animal and Vegetable Fibres.

Animal fibres may be distinguished from vegetable both by their appearance under the microscope and by their chemical reactions. Animal fibres are composed chiefly of protein substances and therefore contain *nitrogen* in addition to carbon, hydrogen, and oxygen, and in the case of wool *sulphur* is also present.

Vegetable fibres consist almost entirely of cellulose $(C_6H_{10}O_5)_n$, or, in some cases, a derivative of cellulose, lignocellulose $(C_{12}H_{18}O_9)_n$; they are therefore of the nature of

carbohydrates. This difference in composition can be shown by the following reactions :—

I. Ignite fibres of wool and silk, and also of cotton and linen (flax) and observe the manner in which they burn.

Animal fibres tend to smoulder and give the characteristic smell of burning nitrogenous matter.

Vegetable fibres burn very readily with no appreciable smell.

II. Heat animal and vegetable fibres in dry test tubes and note that in the case of animal fibres the fumes given off are *alkaline* (due to presence of ammonia), whereas in the case of vegetable fibres the fumes are *slightly acid.*

III. The protein nature of animal fibres may also be shown by means of the *Xanthoproteic* reaction as follows :—

Heat fibres of wool and silk with a little concentrated nitric acid. The solutions become yellow, and on adding excess of ammonia turn brown. This reaction is not given by vegetable fibres.

IV. Animal fibres dye more readily than vegetable fibres ; wool, for example, can often be dyed satisfactorily without using a mordant to fix the colour.

(*a*) Heat fibres of wool, silk, cotton and linen with a solution of picric acid. Remove the fibres from the solution and wash with cold water. The colour is retained on wool and silk, but washes out almost completely from cotton and linen.

(*b*) A similar experiment may be made, using a solution of fuchsine (magenta).

The solution of fuchsine is prepared by dissolving 1 gm. of fuchsine in 100 c.c. of water and adding caustic soda solution until the solution is decolorised. The solution is then filtered and kept in a well-stoppered bottle.

Immerse the fibres to be tested in the solution and warm gently.* Rinse well and then place the fibres in water made slightly acid with acetic acid.

Animal fibres combine with the dye (see p. 93) and will be dyed red (i.e. the original colour of the fuchsine), and vegetable fibres will remain colourless.

V. Animal fibres are much more readily attacked by alkalis than vegetable fibres. This is very important from the point of view of laundry work.

Warm animal and vegetable fibres with a 10 per cent. solution of sodium hydroxide (bench solution may be used).

*Care should be taken not to prolong the heating or the wool will be dissolved.

PLATE I

MICROPHOTOGRAPHS OF FIBRES

(Magnification—approximately 240)

FIG. 1.—Raw wool

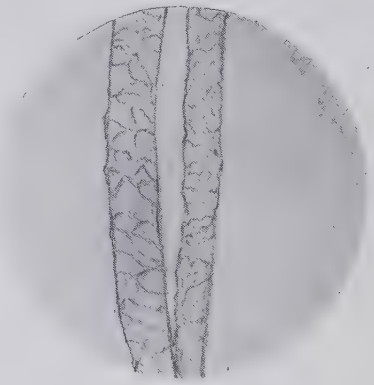


FIG. 2.—Wool

FIG. 3.—Chlorinated wool

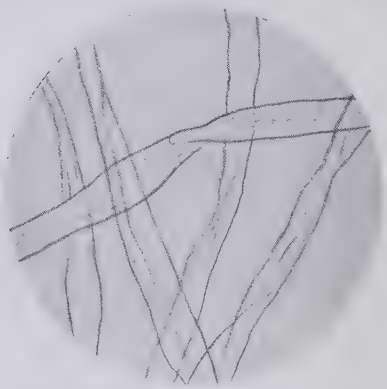


FIG. 4.—Flannelette

FIG. 5.—Raw silk

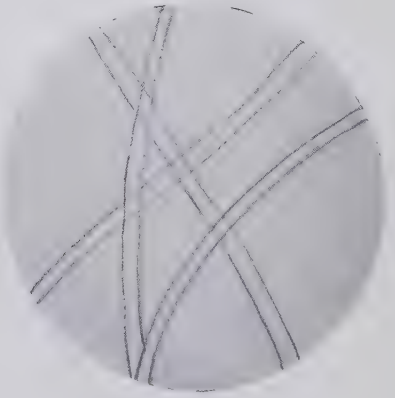


FIG. 6.—Boiled-off silk

[*To face p.* 89

Wool dissolves, giving a yellowish-brown solution.
Silk ,, slowly.
Cotton turns faintly yellow but does not dissolve.
Linen ,, brownish-yellow ,, ,, ,,

WOOL.

Wool is the hair fibre of the sheep. The hair fibres of other animals, e.g. goats, camels, etc., are sometimes used, but to a much more limited extent than those of the sheep.

Raw wool contains a large percentage of impurities. These impurities consist chiefly of:—

(1) *Wool grease*, a fatty substance which serves as a protective coating to the fibres. Raw wool fibres with the grease still attached are shown in Plate I, Fig. 1.

Wool grease contains the alcohol cholesterol ($C_{26}H_{43}OH$) and is the chief source of the product known as "lanoline".

(2) *Suint*, the dried perspiration of the sheep, which consists chiefly of sodium and potassium soaps.

(3) *Vegetable matter*, straw and other vegetable fibres.

(4) *Mineral matter*, clay, grit, etc.

In the ordinary process of wool "scouring," the wool is washed with soap and alkalis (avoiding caustic alkalis, see p. 91). Any vegetable matter still adhering can then be removed by a process known as *carbonising*. The wool is treated with dilute sulphuric acid and then heated to 60°-80° C. The vegetable matter is thus rendered brittle by partial charring and can be shaken out of the wool. (Compare method of determining wool in wool and cotton fabrics, p. 128.) The sulphuric acid is neutralised and washed out. The further mechanical processes of "carding," "spinning" and "weaving" need not be dealt with here.

MICROSCOPICAL APPEARANCE.

Wool is a rounded fibre and shows a characteristic epidermis of horny scales or serrations (see Plate I, Fig. 2). It is to these serrations that the tendency of the fibres to felt is attributed. Coarse wools, with projecting scales, felt much more readily than those approximating to a smooth hair-like structure. For diagrams showing different types of wool see Matthews, "Textile Fibres" (Wiley), and Mitchell and Prideaux, "Fibres Used in Textile and Allied Industries" (Scott, Greenwood).

CHEMICAL REACTIONS OF WOOL.

Wool contains a protein-like substance, *Keratin*, which may be represented by the formula $C_{43}H_{71}O_{13}N_{13}S$; from this an amino acid, *Lanuginic acid*,* may be extracted, and when wool undergoes hydrolytic decomposition a series of other amino acids is obtained.

The presence of an amino group in wool is shown by the fact that ammonia is among the decomposition products obtained when wool is heated (see p. 88, II.). Its presence may also be shown by treating wool with nitrous acid when the wool becomes *diazotised* (see below), and on treatment with alkaline solutions of various phenols a variety of colours can be obtained.

Diazotisation of Wool.

Add a cold solution of nitrous acid (a solution of sodium nitrite acidified with hydrochloric acid) to some white wool fibres.

The wool becomes yellow, and on treatment with boiling water or a solution of caustic soda turns brown.

Some of the diazotised wool should be treated with :—

I. Stannous chloride solution; on warming the colour is discharged.

II. An alkaline solution of (*a*) resorcin, (*b*) *a*-naphthol.

(*a*) resorcin—orange colour turns red with sulphuric acid.

(*b*) *a*-naphthol—red colour ,, black ,, ,, ,,

After treating with the alkaline solution of the phenols the fibres should be washed with water before adding the sulphuric acid.

The Presence of Sulphur in Wool.

This can be shown by warming some wool fibres with a solution of caustic soda and then adding lead acetate solution. A brown colour is produced owing to the formation of lead sulphide.

Silk does not contain sulphur and this, therefore, forms a distinguishing test between silk and wool.

* *Lanuginic acid* is stated by Knecht to have the following composition:— C = 46·1; H = 7·31; N = 10·26; S = 3·35; O = 31·44 per cent.

The Action of Acids on Wool.

When wool is treated with dilute acids it apparently undergoes very little change.

Acids are, however, readily absorbed by wool, and if a woollen fabric is treated with dilute sulphuric acid it is almost impossible to remove all the acid from the fabric by washing only, although the amount of acid actually retained in the wool is very small.

Wool which has been treated with acid is rendered more reactive towards acid dyes. This may be shown by the following experiment.

Warm a piece of white woollen fabric with dilute sulphuric acid, wash with cold water and dye in a solution of picric acid.

Compare the colour with that of a piece of the fabric dyed directly without previous treatment with acid.

Wool dissolves slowly in strong sulphuric acid on heating, but it does not dissolve in the cold. (Compare Silk, p. 96.)

A solution of wool in sulphuric acid has the property of precipitating any of the acid colouring matters from their solution. This fact, when considered in connection with the increased affinity of wool which has been treated with acid for acid dyes, shows that by the action of the acid on wool, there is produced a substance having the property, not previously possessed by wool, of forming lakes with acid colouring matters.

For the action of nitric and nitrous acids on wool see pages 88 and 90.

The Action of Alkalis on Wool.

Wool is rapidly disintegrated by solutions of caustic soda containing from 1-10 per cent. of the alkali (see p. 88, V.).

The action of caustic alkali on wool is much more marked than that of the mild alkalis. This may be shown by warming wool fibres (*a*) with a 1 per cent. solution of caustic soda, (*b*) with a 10 per cent. solution of sodium carbonate, and observing that the action of the alkali is much more marked in (*a*) than in (*b*).

**Mercerised Wool.*—Although wool is rapidly disintegrated by dilute solutions of caustic alkali, stronger solutions increase the strength of the fibres and render it lustrous. The wool is then said to be *mercerised.*

Cover a piece of woollen fabric with a 35 per cent. solution

* For the meaning of the term "mercerised" see page 112.

of caustic soda and allow it to stand for about 5 minutes at the room temperature.

Wash the wool with cold water, dry and note its appearance.

Examine some of the fibres under the microscope; observe that they appear smoother and more transparent than before, and that the scale markings are faint.

The Action of Chlorine on Wool.

The action of chlorine on wool is somewhat peculiar. Wool can be completely decomposed by chlorine gas, or even by a strong solution of chlorine water; but in weak solutions the wool absorbs a considerable quantity of chlorine and becomes altered in character. Wool that has been so treated is rather harsh, has a high lustre and takes on a silk-like "scroop". It loses its felting properties, and its affinity for colouring matters is increased.

The following experiments may be made to show the properties of chlorinated wool.

I. Treat some wool fibres with chlorine water. Wash and dry and examine under the microscope. Bromine water may also be used.

The scales on the epidermis are much less prominent than in the case of untreated fibres (see Plate I, Fig. 3).

This accounts for the loss in felting properties referred to above (see also p. 89).

In comparing fibres of chlorinated and ordinary wool, fibres of each kind may be mounted on the same slide. If the untreated fibres are previously stained with dilute picric acid, they can be distinguished from the others under the microscope and the differences become readily apparent.

II. Treat a piece of woollen material with a solution of alkaline hypochlorite, or bleaching powder, yielding 3-4 per cent. of available chlorine (see Bleaching Agents, p. 135).

Acidify the solution with hydrochloric acid, and after standing a few minutes remove the wool, and rinse thoroughly with cold water. Finally, wash the wool with soap and water, rinse and dry.

The appearance and feel of the fabric should be carefully observed. If a drop of water is allowed to fall on the chlorinated fabric, the drop is absorbed, forming a circular spot; whereas in the case of ordinary wool the drop retains its shape for a considerable time, and when finally absorbed by the fabric the wetted portion is irregular in shape.

The chlorinating of wool, as described above, is made use of in the production of unshrinkable woollens. Experience, however, shows that such materials usually wear badly.

III. Dip pieces of chlorinated and untreated wool into a dilute solution of methyl violet and warm gently.

Rinse well with cold water, dry and compare the colours.

The chlorinated wool takes up more colour than the untreated wool.

Two colour effects in woollen fabrics are sometimes obtained by weaving together threads of chlorinated and untreated wool, and dyeing the fabric thus obtained.

Wool which is to be dyed black is also sometimes treated with chlorine in order to increase the depth of colour.

The Dyeing of Wool.

The affinity of wool for dyes and colouring matters has already been dealt with in the course of the above experiments.

Wool, it should be noted, is, as regards colouring matters, the most reactive of all the textile fibres. It combines directly with both acid and basic dyes, and this is attributable to the presence of groupings characteristic of the amino acids (see p. 90). The wool therefore exhibits both acid and basic properties.

If glycine be taken as a typical example of an amino acid the reaction with acids and bases can be illustrated by the following equations:—

$$\underset{\text{Amino acid.}}{CH_2NH_2COOH} + \underset{\text{Acid.}}{HCl} \rightarrow \underset{\text{Hydrochloride of acid.}}{CH_2NH_2\begin{matrix}HCl\\ \diagup\\ \diagdown\\ COOH\end{matrix}}$$

$$\underset{\text{Amino acid.}}{CH_2NH_2COOH} + \underset{\text{Base.}}{NaOH} \rightarrow \underset{\text{Sodium salt of acid.}}{CH_2NH_2COONa} + H_2O$$

Detection of Dyed Fibres.—Wool fibres dyed to resemble those of the natural yellowish-brown tint are best detected by the microscope. A brilliant (daylight) illumination should be used and the iris diaphragm should be wide open.

Under these conditions the pigment particles in the natural coloured fibres will be clearly seen as dots or broken lines, suggesting an interrupted or stippled colour surface.

Artificially coloured fibres exhibit under these conditions an absolutely uniform colour, and can therefore be distinguished from the natural fibres however nearly the tint may be matched.

Hygroscopic Character of Wool.

Wool is very hygroscopic and exhibits this property to a more marked extent than any of the other textile fibres.

The amount of moisture in wool varies considerably according to the humidity and temperature of the surrounding atmosphere. Under average conditions it is usually from 12-14 per cent.

Since wool is sold by weight on a large scale, sales have to be based on the proportion of moisture in the wool, and the official processes for determining this amount are termed "*conditioning*". (For further details of these processes see Matthews, "Textile Fibres" (Wiley).)

In making quantitative experiments with fabrics containing wool, precautions should be taken to ensure that the fabric is weighed under the same atmospheric conditions, before and after the experiment.

For this reason wool which has undergone any process involving washing and subsequent drying should be allowed to stand for some considerable time at the room temperature before reweighing, so that the moisture content may be the same as in the first weighing. All the weighings should, if possible, be carried out on the same day.

If more accurate results are required, the fabric should be dried at 100° C. to constant weight both before and after the experiment, and weighed in a stoppered vessel.

Silk.

Silk is obtained from the cocoons of a species of caterpillar (*Bombyx mori*) which feeds upon the leaves of the mulberry tree.

In making the silk, the silk-worm secretes a viscous fluid, *fibroin*, from two glands in its body and forces this liquid through two minute channels in its head into a single exit tube. Two other glands deliver into the same exit tube a cementing or fixing fluid, *sericin*. As it emerges from the head of the silk-worm the fibroin coagulates, forming a double filament coated with sericin (see Plate I, Fig. 5).

Besides the mulberry silk-worm (*Bombyx mori*) there are other varieties of caterpillars, which also produce silk in sufficient quantity to be of commercial importance. These silk-worms are not capable of being cultivated like the mulberry

PLATE II

MICROPHOTOGRAPHS OF FIBRES

(Magnification—approximately 240)

FIG. 7.—Wild silk

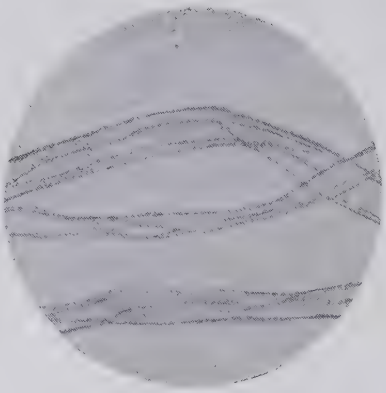


FIG. 8.—Cotton

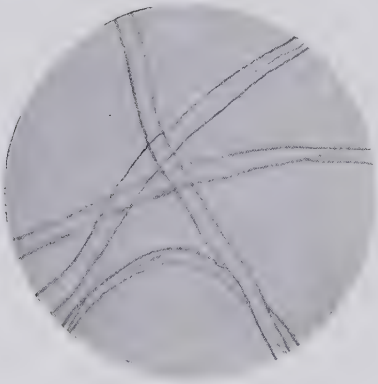


FIG. 9.—Mercerised cotton

FIG. 10. -Lustra-cellulose (viscose)

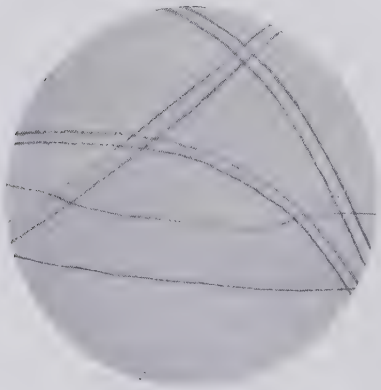


FIG. 11.—Silk and lustra-cellulose

FIG. 12.—Linen

[*To face p.* 95

silk-worm, and for this reason the silk obtained from these caterpillars is called *wild silk;* the most important is *Tussah silk.*

Raw silk contains about 75 per cent. of real silk, i.e. fibroin, and about 25 per cent. of sericin, sometimes called "silk gum" or "silk glue". This latter substance is soluble in hot water, forming a jelly on cooling, and is therefore also termed "silk gelatine".

In preparing silk for use, part or all of the sericin is removed by a hot solution of soap and water, and this process is described as "*degumming*" or "*boiling-off*".

If the silk is completely "boiled off" * it loses from 20-25 per cent. of its weight and becomes soft and glossy. The soap solution containing the sericin (boiled-off liquor) is subsequently used in the dye bath as an assistant in fixing the colour.

Properties of Silk Fibres.—Silk fibres are characterised by extreme fineness and great length. The diameter of the cocoon threads is about 0·0005-0·0007 inch, or, expressed in another form, there are from 1430-2000 threads to the inch. These threads are often from 1300-1400 yds. long. Silk has a high lustre and great tensile strength and elasticity. The tensile strength of a silk thread is said to be almost equal to that of an iron wire of the same diameter.

MICROSCOPICAL APPEARANCE.

Raw silk is seen under the microscope to consist of a double filament coated irregularly with particles of sericin (see Plate I, Fig. 5).

Boiled-off silk appears as a fine, rounded fibre, devoid of structure and of fairly uniform thickness (see Plate I, Fig. 6).

If examined under polarised light very fine colour effects are obtained.

Wild Silks.—The microscopical appearance of wild silks is quite different from that of true silk (*Bombyx mori*). The fibres are broad and flat and show considerable variations in width. Longitudinally the fibres exhibit distinct striations and also peculiar cross markings, usually running obliquely across the fibre (see Plate II, Fig. 7).

* *Boiled-off silk* is the term used to describe silk which has lost from 20-30 per cent. of its weight during the degumming process.

Souple silk is silk which has only lost from 8-12 per cent. of its weight and therefore still contains a considerable proportion of the sericin.

Ecru silk is silk which has only lost from 3-4 per cent. of its weight and therefore still contains nearly all the sericin.

The striated appearance of wild silk is evidence that structurally the fibre is composed of minute filaments.

The appearance of wild silk under polarised light is also different from that of true silk.

CHEMICAL REACTIONS OF SILK.

The two principal constituents of silk are, as already noted, fibroin and sericin; both these are protein substances and contain amino acid groups.

The silk fibres obtained after boiling off the sericin are composed almost entirely of fibroin.

The formulæ obtained for fibroin by different observers vary considerably, and the fibroin of wild silk appears to differ somewhat from that of ordinary silk. In this connection it may be noted that wild silks are more resistant than ordinary silk to the action of acids and other solvents (see below).

Fibroin, unlike the protein in wool, does not contain sulphur, and methods of distinguishing between the two fibres in mixtures have been based on this fact.

The presence of an amino group in silk may be shown by means of the reactions described in the case of wool (p. 90).

The Action of Acids on Silk.

Strong acids dissolve silk more or less rapidly, while weak organic acids are readily absorbed.

Sulphuric acid dissolves silk in the cold, but if allowed to act for a short time only causes a contraction of the fibre.

Wild silk, e.g. tussah, is affected to a much less extent, and this fact is made use of in producing silk crapes by the action of sulphuric acid on mixtures of silk and tussah silk.

Treat specimens of silk (white washing)* and tussah silk with sulphuric acid (concentrated acid diluted equal parts with water), and observe that the true silk dissolves more readily than the tussah silk.

Hydrochloric Acid.—Silk dissolves in strong hydrochloric acid in the cold, and this is made use of in separating silk from cotton and wool in mixtures (see p. 131), and also in examining silk for weighting (see p. 100).

Nitric Acid (see p. 88, III.).

Nitrous Acid.—Action similar to that on wool (see p. 90).

* White washing silk usually contains very little weighting and may therefore be used for showing the reactions of silk.

Hydrofluoric Acid.—A dilute solution of hydrofluoric acid (5 per cent.) does not attack silk to any marked extent, and this acid is sometimes used for extracting the weighting materials from silk (see p. 103).

Tannic Acid or Tannin.—Silk readily absorbs tannic acid, and this absorption is made use of in the dyeing and weighting of silk (see p. 98).

To show the absorption of tannic acid by silk, warm a piece of white silk in a solution of tannic acid, wash well with water and then immerse the silk in a solution of ferric chloride. A dark coloration is produced on the silk by the formation of iron tannate.

The Action of Alkalis on Silk.

Hot, concentrated solutions of caustic alkali dissolve silk (see p. 88, V.), but it is not affected by dilute alkalis to the same extent as wool. This may be shown by comparing the action of a 1 per cent. solution of caustic soda on wool and on silk fibres.

Sericin, it should be noted, is readily soluble in dilute alkalis including ammonia. (See also removal of sericin by action of soap and water, p. 95.)

The Action of Other Reagents on Silk.

Fibroin is soluble in an ammoniacal solution of copper oxide (cuprammonium solution), but sericin does not dissolve. Hence "boiled-off" silk dissolves in this reagent, and in the case of raw silk the fibroin dissolves, leaving the sericin.

An alkaline solution of copper oxide containing glycerine dissolves silk, but is without action on lustra-celluloses (see p. 119, also p. 133). Silk is also soluble in a boiling solution of basic zinc chloride (Elsner's reagent), and this reagent is used for dissolving out the silk from a mixed fabric (see p. 133).

Silk is rapidly destroyed by the action of *chlorine*, and bleaching powder and solutions of hypochlorites should not be used for bleaching silk fabrics.

The above-mentioned solutions are prepared as follows:—

Ammoniacal Copper Oxide (Cuprammonium) Solution or Schweitzer's Reagent.—Dissolve 5 gms. of copper sulphate in 100 c.c. of water. Add caustic soda to precipitate the cupric

hydroxide, filter, wash the precipitate several times with cold water and then dissolve it in the least possible quantity of ammonia.

Alkaline Copper-glycerine Solution.—Dissolve 10 gms. of copper sulphate in 100 c.c. of water, add 5 gms. of glycerol and just sufficient caustic soda to dissolve the precipitate of copper oxide at first obtained.

Basic Zinc Chloride Solution (*Elsner's Reagent*).—Dissolve 500 gms. of zinc chloride and 20 gms. of zinc oxide in 425 c.c. of water and warm until a clear solution is obtained. The liquid becomes turbid on standing in the cold, but clears again on heating.

The Dyeing of Silk.

Silk takes up dyes readily from a solution and resembles wool in behaving both as an acid and as a base; this is attributed, as in the case of wool, to the presence of groups characteristic of amino acids (see p. 93).

Hygroscopic Character of Silk.

Silk absorbs moisture very readily, and in selling silk by weight the methods adopted are similar to those used in the "conditioning" of wool (p. 94). Under normal conditions silk contains 10-12 per cent. of water.

"Boiled-off" silk is not so hygroscopic as "raw silk".

In weighing silk for quantitative experiments the same precautions should be adopted as in the case of wool (p. 94).

THE WEIGHTING OF SILK.

The practice of adding to the weight of silk, during the dyeing and finishing processes, is now so general that the detection and determination of the character and amount of the "weighting" in silk is a matter of considerable practical importance.

Dark coloured, especially black silks may be loaded with iron tannate (see p. 97) or Prussian blue. These substances, besides increasing the weight of the material, also act as mordants and help to fix the colouring matter.

Light coloured silks cannot be weighted with the above-mentioned substances owing to the dark colours produced. Such silks were formerly weighted with soluble substances,

e.g. cane sugar, glucose, magnesium salts, gelatine, etc., but at the present time these silks are usually weighted with insoluble compounds of tin, and this method is now also frequently employed for dark coloured silks.

One of the most common methods of weighting with tin is by treatment with a solution of stannic chloride, followed by treatment with solutions of phosphates and silicates, whereby the tin is precipitated in the fabric as insoluble phosphate and silicate of tin.

The weighting of silk may be demonstrated on a small scale by the following experiments :—

I. Weighting of Silk by the Tin Silico-Phosphate Method.

Prepare the following solutions :—

(*a*) Dissolve 40 gms. of stannic chloride ($SnCl_4 . 5H_2O$) or 30 gms. of anhydrous stannic chloride in 70 c.c. of water.

(*b*) Dissolve 13 gms. of sodium phosphate

($Na_2HPO_4 . 12H_2O$) in 87 c.c. of water.

(*c*) Dilute "water-glass" with water to a specific gravity of 1·04.

Weigh out a piece of white washing silk (about 2 gms.). Immerse the silk in solution (*a*) for one hour.

Heat solutions (*b*) and (*c*) to a temperature of 60° C. Remove the silk from solution (*a*), rinse with water and immerse in solution (*b*) for 10 minutes and then in solution (*c*) for the same length of time. Rinse well with water and repeat the whole process, finally dry and weigh. (For precautions to be taken in weighing see p. 94.)

II. Weighting of Silk by Iron Tannate.

Prepare the following solutions :—

(*a*) Dissolve 10 gms. of commercial tannic acid in 100 c.c. of water.

(*b*) Dissolve 10 gms. of ferric nitrate in water; or if ferric nitrate is not available prepare a solution of ferric acetate by adding 15 gms. of sodium acetate to a solution containing 10 gms. of ferric chloride in 100 c.c. of water.

Weigh out a piece of white washing silk (about 2 gms.).

Heat the iron solution to 70-80° C. and immerse the silk in it for about 10 minutes.

Squeeze out the silk, transfer to the tannic acid solution and heat to boiling for a few minutes.

Repeat the treatment in both solutions two or three times, finally rinse well with water, dry and weigh.

(For precautions to be taken in weighing see p. 94.)

In both experiments the silk will be found to have increased in weight.

Detection of Weighting in Silk.

The complete examination of a silk fabric, for all the substances which may possibly be present, involves several long and somewhat complex processes, but an examination carried out on the lines described below will show the nature of the principal weighting substances present and illustrate the methods most usually employed.*

Preliminary Tests.—Pure silk contains less than 1 per cent. of ash and burns readily. Silk which has been weighted and which, therefore, contains a considerable quantity of mineral matter burns much less readily.

Ignite a piece of silk and note the appearance of the ash obtained. If the silk burns slowly and gives an ash which retains the original structure of the fabric the silk has been weighted.

Pure silk dissolves readily in hydrochloric acid (see p. 96). Weighted silks dissolve much less readily. This difference is more marked with silks weighted with tin than with those weighted with iron (except in the case of those weighted with Prussian blue, see p. 101).

Treat a piece of the material with concentrated hydrochloric acid. If the silk is not weighted it will dissolve rapidly in the cold.

If the above reactions indicate that the silk is weighted the nature of the weighting materials should then be investigated.

As already indicated (p. 98) the most usual methods of weighting silk are :—

(1) By iron, as ferrocyanide or tannate (dark silks only).

(2) By tin, as tannate, phosphate or silicate.

* For further details of the detection and determination of weighting in silk see Allen's "Commercial Organic Analysis," Vol. VIII., and "Technical Methods of Chemical Analysis," Lunge (Keane).

Dissolve some of the silk in concentrated hydrochloric acid.

If a white gelatinous precipitate is obtained the presence of silicate is indicated. Filter off the precipitate (if any) and examine portions of the solution as follows:—

Detection of Iron.—Add potassium ferrocyanide to the solution; a precipitate of Prussian blue shows the presence of iron.

$$3K_4Fe''(CN)_6 + 4Fe'''Cl_3 \rightarrow Fe_4'''(Fe(CN)_6)_3 + 12KCl$$

Potassium ferrocyanide. — Ferric ferrocyanide Prussian blue.

If the iron was originally present in the silk entirely in the form of Prussian blue it cannot be detected by means of the above reaction, since Prussian blue is insoluble in hydrochloric acid.

A special test for the presence of Prussian blue is given below.

Detection of Tin.—Dilute the hydrochloric acid solution, pass sulphuretted hydrogen through it and warm. If tin is present a yellow precipitate of tin sulphide will be obtained.

Detection of Phosphate.—Neutralise a small portion of the solution with ammonia, acidify with a few drops of nitric acid, add a considerable excess of ammonium molybdate solution and warm. A yellow precipitate shows the presence of a phosphate.

Detection of Tannin.—The tannin in silk is usually present in the form of insoluble lakes, i.e. compounds with iron or tin, and before testing, the tannin must first be liberated by the action of hydrochloric acid.

A portion of the hydrochloric acid solution of the silk (after dilution) should be tested for tannin by adding excess of sodium acetate and a few drops of ferric chloride solution. A dark blue-black coloration shows the presence of tannin.

Detection of Prussian Blue.—If the silk is dark in colour, it should be examined for the presence of Prussian blue.

Prussian blue though not dissolved in hydrochloric acid is readily decomposed by alkalis, thus:—

$$Fe_4'''(Fe(CN)_6)_3 + 12NaOH \rightarrow 4Fe'''(OH)_3 + 3Na_4Fe(CN)_6.$$

Treat the silk with dilute sodium hydroxide solution. Pour off the alkaline solution, acidify with hydrochloric acid and add a few drops of ferric chloride. Prussian blue, if originally

present, will be reformed, since the alkaline solution (see equation, p. 101) contains the ferrocyanide extracted from the silk (see equation, p. 101).

The Determination of Weighting in Silk.

The quantity of weighting material in a silk may be determined in several different ways. The methods used depend, either on finding the amount of real silk (fibroin) present in the fabric, or on finding the amount of material other than silk present in the fabric.

The determinations are usually made on air-dry silk (i.e. silk which is weighed when dry at the room temperature).* Under these conditions the silk will contain 10-12 per cent. of moisture (see p. 98), and, for the purposes of calculation, it is usual to assume that air-dry silk contains 11 per cent. of moisture.

The loss in weight during the "boiling-off" of silk is about 20-25 per cent. (see p. 95), and the addition of weighting materials to the extent of 25 per cent. to compensate for this loss is considered a legitimate practice in the trade. For this reason the amount of weighting is usually calculated on the raw silk and not on the "boiled-off" silk, and the weighting is expressed as "*percentage above 'pari'*" or "*par*". For example, if the weight of 100 gms. of raw silk is reduced to 75 gms. by boiling-off, and is then increased to 135 gms. during the dyeing and finishing processes, the silk is described as being weighted 35 per cent. above "pari".

In the United States of America the weighting is expressed "as ounces of weighting" added to each pound of *raw* silk. Thus weighting of 30/32 indicates that from 16 ozs. of raw silk 30-32 ozs. of weighted silk were produced.

Sixteen ozs. of raw silk are taken as equivalent to 12 ozs. of "pure" or "boiled-off silk".

(For further details and table for conversion of percentage weighting to ounces per pound, see "Textile Fibres," Matthews.)

The methods most commonly employed for the determination of the amount of weighting in a silk are as follows :—

(1) *Determination of the amount of nitrogen in the material* by Kjeldahl's process (see Vol. II.), after the removal of all nitrogenous weighting materials, e.g. Prussian blue, ammonium salts, etc.

* See also pages 94 and 127.

From the percentage of nitrogen thus obtained the quantity of real silk (fibrion) can be calculated.

Pure boiled-off silk, containing 11 per cent. of moisture, contains 17·6 per cent. of nitrogen. Therefore every gram of nitrogen found in the fabric represents 100 ÷ 17·6 = 5·68 gms. of air-dry silk (fibroin).

(For further details of this method see "Textile Fibres," Matthews; also Allen's "Commercial Organic Analysis," Vol. VIII.)

(2) *Determination of the weight of real silk present* by removing all the weighting materials by the action of hydrofluoric acid.

As already noted (p. 97), silk is not appreciably affected by the action of a 5 per cent. solution of hydrofluoric acid, but the weighting materials may be dissolved out by the action of this acid, and the residual silk can then be washed, dried and weighed.

The determination may be carried out in the following manner :—

About 2 gms. of air-dry silk are immersed for 1 hour in 100 c.c. of a 5 per cent. solution of hydrofluoric acid, in a platinum dish, at the room temperature.

The silk should be stirred by means of a platinum wire, and turned over at frequent intervals. The treatment is then repeated with 100 c.c. of fresh acid of the same concentration, and the silk is finally washed several times with distilled water dried and weighed (see p. 94).

The loss in weight of the fabric gives the amount of weighting present.

(For method of calculating weighting added to raw silk see p. 104.)

(3) *Determination of the amount of mineral matter present* by ashing.

If all the organic matter in the silk is removed by incineration, the weight of residue will represent the amount of mineral matter added to the silk, since the ash of pure silk is under 1 per cent.

This method of determining the amount of weighting added to a silk is easy of execution and gives good results, except in the case of silks weighted with tannin or other organic matter (see p. 100).

Tannin and other organic weighting will be decomposed, together with the silk, during the process of incineration ; the

weight of the ash does not, therefore, in such cases represent the total amount of weighting material added to the silk, and one of the other methods previously described should be employed.

A determination of the amount of weighting materials in a silk *not* weighted with tannin or other organic matter can be carried out in the following manner :—

Weigh out about 2 gms. of air-dry silk, and cut it into small strips.

Ignite each strip separately in a Bunsen flame and when it ceases to burn transfer it to a weighed crucible.

When all the silk has been so treated heat the crucible with a good Bunsen flame until the ash is white or uniform in colour.* Cool in a desiccator and weigh. Heat the crucible again for about fifteen minutes, cool and weigh. If the weight is not constant, the heating must be continued until a constant weight is obtained.

The weight of ash gives the weight of added mineral matter.

Method of calculating the "percentage of weighting above 'pari'" or above "par".—If the amount of weighting in a silk has been determined by one of the above methods, the percentage of weighting above "pari" can be calculated as shown in the following examples :—

The weighting is usually stated with reference to raw silk containing 11 per cent. of moisture, and if the origin of silk is unknown, it is assumed that the loss on "boiling-off" is from 20-25 per cent. It may for the purposes of calculation be taken as 22 per cent. (see p. 102).

Example I.

1·820 gms. air-dried silk (containing 11 per cent. moisture) gave 0·942 gm. real silk fibroin (air-dry).

By difference the weighting = 1·820 − 0·942 gm.
= 0·878 gm.

Taking the loss due to boiling-off as 22 per cent., 78 parts of fibroin correspond to 100 parts of raw silk.

Since the weighting added to 0·942 gm. of fibroin = 0·878 gm.,

the weighting added to 78 gms. of fibroin $= \frac{0{\cdot}878 \times 78}{0{\cdot}942}$ gms.

$= 72{\cdot}7$ gms.

* If the silk is weighted with iron the ash will be reddish-brown in colour owing to the presence of Fe_2O_3.

The silk as sold is composed of 78 parts of fibroin + 72·7 parts of weighting = 150·7 parts of weighted silk.

Or since 78 parts of fibroin correspond to 100 parts of raw silk, 150·7 parts of weighted silk have been produced from 100 parts of raw silk, and the silk is therefore weighted 50·7 *per cent. above par.*

Example II.

2·00 gms. of air-dried silk (weighted only with inorganic substances, see p. 104) gave 0·725 gm. of ash.

By difference weight of fibroin = 2·00 − 0·725 = 1·275. Therefore, weighting added to 1·275 gms. fibroin = 0·725. The method of calculation is then the same as in the previous example and the silk is found to be weighted 22·4 per cent. above "pari".

Determination of Silicate and Tin in the Ash of Silk.

If a previous examination of the silk has shown that it contains tin and silicate, the quantities of these substances present in the ash can be determined in the following manner :—

Add to the ash, obtained as described above, about six times its own weight of fusion mixture and a little powdered potassium nitrate and mix thoroughly. Heat the mixture in a crucible until the mass is well fused. Cool and when cold place the crucible on its side in a porcelain dish. Pour some distilled water into the dish and cover with a clock glass. Warm the dish and keep the water just boiling until the melt has completely softened (i.e. until all the lumps have broken up) and detached itself from the crucible.

Remove the crucible from the dish and carefully wash off the adhering solution and any small particles of solid into the dish. Warm the contents of the dish, filter, wash the residue several times with hot water and collect the filtrate and washings. By the process of fusion with alkaline carbonates and subsequent extraction with water the tin and silicate are obtained in solution in the form of sodium and potassium stannate ($K_2O \cdot SnO_2$) and sodium and potassium silicate respectively. Iron, if present, will be in the residue and, if desired, the quantity present can be determined by dissolving the residue in hydrochloric acid and finding the amount of iron either by a gravimetric or by a volumetric method.

Determination of Silicate as SiO_2—Acidify the solution with hydrochloric acid, evaporate to dryness and proceed as described on p. 40; being careful to collect all the filtrate and washings.

*Determination of Tin as Dioxide** (SnO_2).—Saturate the filtrate, obtained after the removal of the silica, with hydrogen sulphide gas. Cover the vessel with a clock glass and allow it to stand in a warm place until the smell of hydrogen sulphide has almost disappeared. Filter, wash the precipitate and dry in a steam oven.

Detach the precipitate as completely as possible from the filter paper and transfer it to a weighed crucible. Burn the filter paper separately, and when ashed add it to the contents of the crucible.

Heat the crucible gently for some time with the lid on, then remove the lid and continue heating until the smell of sulphur dioxide is no longer perceptible.

Finally, heat the crucible to a bright red heat until a constant weight is obtained. In this way the tin sulphide is completely converted into tin oxide and is weighed as such.

The percentage of tin oxide in the ash or in the fabric can then be calculated.

Cotton.

Cotton fibres are the seed hairs of the cotton plant (*Gossypium*) which grows as a shrub in warm climates.

The seed hairs are enclosed with the seeds in a pod or "*boll*". On ripening, the boll bursts open showing a mass of white downy fibres with the cotton seeds embedded in them. The seeds are separated from the fibres by a process known as "*ginning*".

The seeds are of special value on account of the oil which they contain (cotton-seed oil) which is used in the manufacture of soap and margarine (see p. 55 and Vol. II.). The husks of the seeds are also utilised in the production of cattle fodder and manures.

Raw cotton fibres are covered with a waxy coating which is removed from the fibres, after they have been spun into threads, by boiling with a dilute solution of caustic soda under slightly increased pressure.

The wax is not soluble in the alkaline solution, but is separated from the fibres by a process of emulsification.

Cotton fibres are comparable in diameter with silk or fine

* The tin is precipitated from solution as sulphide (SnS_2) and is converted into oxide by heating until all the sulphur has been expelled as SO_2

$$SnS_2 + 3O_2 \rightarrow SnO_2 + 2SO_2.$$

wool fibres, but are considerably shorter than silk, wool or flax fibres.

MICROSCOPICAL APPEARANCE.

The cotton fibre consists of a single cell; during growth the inner tube or lumen is filled with a liquid and the fibre is cylindrical in shape. As the fibre ripens the cell contents gradually dry and the fibre flattens irregularly, presenting the appearance of a twisted ribbon with thickened edges (see Plate II, Fig. 8).

CHEMICAL REACTIONS OF COTTON.

About 91 per cent. of the cotton fibre consists of cellulose (empirical formula $C_6H_{10}O_5$), the other constituents being water, about 8 per cent., cotton wax 0·3-0·5 per cent. (see p. 106), and small amounts of mineral matter and natural colouring matter.

If raw cotton is treated successively with dilute caustic soda, dilute acid, water, alcohol, and ether, chemically pure cellulose is obtained, and the chemical reactions of cotton may therefore be regarded as illustrating also the behaviour of pure cellulose, under similar conditions.

Cellulose belongs to the class of organic substances known as *carbohydrates*, and is therefore closely allied to starch and to the sugars.

Its exact molecular structure has not yet been determined, but its reactions show that it contains both hydroxyl (– OH) and carbonyl (= CO) groups, and its formula should be expressed as $(C_6H_{10}O_5)_n$ where n is some whole number of which the value is at present unknown.

The Action of Acids on Cotton.

Cotton is not dissolved by cold, dilute solutions of acids, but if cotton which has been treated with dilute acids is dried without any intermediate process of washing to remove the acid, the cotton becomes "tendered," i.e. is converted into a friable substance which readily falls to pieces.

This is due to the concentration of the acid on the fabric on drying, and the formation of a hydrated cellulose probably of the form $2C_6H_{10}O_5 . H_2O$.

This behaviour of cellulose with dilute acids is made use

of in the separation of cotton from mixed fabrics of cotton and wool (see p. 128), and also in the "carbonising" process for removing vegetable matter (chiefly cellulose) from raw wool (see p. 89).

It is also important to remember that if a cotton fabric has, during any process of dyeing, bleaching, etc., been treated with solutions containing free acid, the acid must be completely removed from the fabric before drying, either by thorough washing, or by neutralising with dilute alkali; otherwise the fabric will be tendered and possibly destroyed.

The following experiment may be made to show the action of dilute acid on cotton:—

Immerse two pieces of cotton fabric in dilute hydrochloric acid (1 part of concentrated acid to 8 of water), and allow them to stand at the room temperature for about ten minutes. Remove them from the solution; dry one piece without washing (preferably in front of a fire or stove). Wash the other piece thoroughly with water and then dry.

The cotton which was washed before drying will be very little affected by the action of the acid, whereas the other piece will darken considerably on drying, and will readily fall to pieces on rubbing.

Action of Sulphuric Acid.—Concentrated sulphuric acid dissolves cotton in the cold, and on diluting with water a white amorphous substance, *amyloid* ($C_{12}H_{22}O_{11}$), separates out, which, like starch, gives a blue colour with iodine.

Amyloid is used in the production of "vegetable" parchment; its formation and reaction with iodine may be shown in the following manner:—

Dip a piece of filter paper, which should be free from starch dressing, into strong sulphuric acid for a few seconds. Place in a porcelain dish and wash well with water. Drain off the water, moisten the paper with a few drops of iodine solution and wash again. The paper is stained blue. Carefully dry the paper and observe its parchment-like texture and appearance. The cellulose of which the paper is composed has been coated with a layer of amyloid.

On boiling with dilute sulphuric acid, cotton is converted into dextrin and glucose.

Dissolve a piece of cotton in a mixture of equal parts of strong sulphuric acid and water. Dilute the solution and boil for some little time, until a clear solution is obtained. Test portions of the solution for glucose and dextrin.

Test for Glucose.—Neutralise the solution with sodium carbonate, add Fehling's solution and boil (see Vol. II.).

Test for Dextrin.—Add to the solution two or three times its own volume of alcohol; dextrin, if present, will be thrown down as a white precipitate (see Vol. II.).

Action of Hydrochloric Acid.—This in dilute solutions is similar to that of sulphuric acid; but concentrated hydrochloric acid does not dissolve cotton in the cold (see p. 108).

Action of Nitric Acid.—When boiled with moderately strong nitric acid (sp. gr. 1·1-1·2), cotton is converted into *oxycellulose*, a structureless, friable substance, which is also obtained by the action of other oxidising agents on cellulose. (Compare action of chlorine on cotton, p. 112.)

Concentrated nitric acid (sp. gr. = 1·42) reacts with the hydroxyl groups of the cellulose molecule with the formation of nitric esters, or so-called nitrocelluloses.*

The reaction with nitric acid is more complete in the presence of sulphuric acid, which acts as a dehydrating agent. The "degree of nitration," i.e. the number of nitro groups taken up by the cellulose molecule, depends on the concentration of the acid, the temperature, and the duration of the process. The formation of cellulose dinitrate may be shown by the following equation:—

$$\dagger\ \underset{\text{Cellulose.}}{C_{12}H_{18}O_8(OH)_2} + 2HNO_3 \rightarrow \underset{\text{Cellulose dinitrate.}}{C_{12}H_{18}O_8(ONO_2)_2} + 2H_2O$$

The following are some of the more important compounds which may be obtained by the action of nitric acid on cellulose; they are sometimes classified under the general name of *pyroxylins*:—

Cellulose hexanitrate or hexanitrocellulose (gun cotton)		$C_{12}H_{14}O_4(ONO_2)_6$
,,	pentanitrate or pentanitrocellulose	$C_{12}H_{15}O_5(ONO_2)_5$
,,	tetranitrate ,, tetranitrocellulose	$C_{12}H_{16}O_6(ONO_2)_4$
,,	trinitrate ,, trinitrocellulose	$C_{12}H_{17}O_7(ONO_2)_3$
,,	dinitrate ,, dinitrocellulose	$C_{12}H_{18}O_8(ONO_2)_2$

The "nitrocelluloses" are all very inflammable; the inflammability increases with the number of nitro groups

* It should be noted that the action of nitric acid on cellulose is comparable with that of the action of this acid on glycerol. Nitrates are produced and not true nitro-compounds.

† In writing the formulæ of cellulose nitrates it is usual to adopt $C_{12}H_{20}O_{10}$, or $2(C_6H_{10}O_5)$ as the molecular formula of cellulose (see p. 107).

present, and hexanitrocellulose or gun cotton is used largely in the manufacture of explosives (propellants).

Hexanitrocellulose is insoluble in a mixture of alcohol and ether, and in this respect differs from the other nitrocelluloses which dissolve in a mixture of alcohol and ether, forming a solution known as *collodion.*

Celluloid is obtained by dissolving nitrocelluloses in molten camphor, the mixture obtained being highly inflammable.

The formation of nitrocelluloses from cotton and some of their more important reactions may be shown by means of the following experiments :—

Immerse a piece of absorbent cotton (i.e. "cotton wool") for about one minute in a well-cooled mixture of 1 part of concentrated nitric acid with 2 parts of concentrated sulphuric acid. Wash the cotton well and allow it to dry on a filter paper at the room temperature (well away from any flame).

Take a small piece of nitrated cotton and place it on an iron tray together with a piece of untreated cotton.

Ignite both pieces and observe that the nitrated cotton is more inflammable than the untreated cotton.

Treat the remainder of the nitrated cotton with a mixture of alcohol and ether, shake gently for a few minutes.

The nitrated cellulose will dissolve, and a residue of unchanged cotton will be left undissolved. Pour off a few drops of the solution on to a glass plate and allow the plate to stand at the room temperature until the solvent has evaporated. (The whole operation should be carried out well away from any flame.)

The nitrocellulose will be deposited on the plate as a coherent transparent film. This film (collodion) is impermeable to air and water and is utilised in surgery and in photography.

Collodion is also used in the preparation of artificial silk by the Chardonnet process (see p. 116).

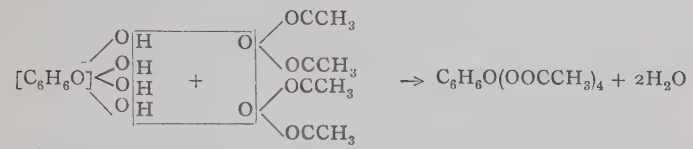
Action of Hydrofluoric Acid.—When cotton is treated with hydrofluoric acid a tough transparent waterproof material is obtained.

This substance is used in the manufacture of carbon filaments for electric lamps and also as an insulating material.

Organic Acids have very little action on cotton, but tannic acid is readily absorbed by it, advantage being taken of this in the dyeing and mordanting of cotton. (Compare action of tannic acid on silk, p. 97.)

Acetic Anhydride.—By the action of acetic anhydride and sulphuric acid a number of different acetates of cellulose can be produced; the number of acetyl groups introduced into the molecule depends on the conditions of the experiment. (Compare nitration of cellulose, p. 109.)

The formation of the tetracetate may be shown by the following equation:—



Cellulose. Acetic anhydride. Cellulose tetracetate.

Commercially, cellulose acetate is used for a number of different purposes; when mixed with camphor it yields a material which resembles and is, in many respects, superior to celluloid and which is not inflammable.

This substance, known as "*cellon*," is used as a substitute for guttapercha, vulcanite, etc., and also in the manufacture of kinematograph films.

Cellulose acetate is soluble in certain organic solvents, e.g. acetone and chloroform, and is employed in the form of a thick viscous solution as a flexible varnish for wood, paper and metal, and is used extensively for coating the wings of aircraft.

A form of artificial silk ("*cellestion*" silk) can be prepared from cellulose acetate, which on account of its high insulating properties is used for coating electric wires.

The Action of Alkalis on Cotton.

Dilute solutions of alkali under ordinary conditions have very little action on cotton (see p. 88, V.); but prolonged boiling with alkalis in the presence of air causes hydrolysis of the cellulose, the action being similar to that of acids (see p. 108). In the absence of air the action is much less marked.

Concentrated solutions of caustic alkali (30 per cent.) have a curious effect on cotton; the fibres contract in length, but swell up and become cylindrical in shape, and their tensile strength and affinity for colouring matters are increased.

The alkali reacts chemically with the cellulose forming *alkali-cellulose*, a compound in which the molecular ratio of alkali to cellulose may be expressed as $C_{12}H_{20}O_{10} : NaOH$.

This action of alkali on cellulose forms the basis of the

process known as "mercerising," so called after John Mercer, who in 1844 first suggested that the action of concentrated alkali on cotton might be utilised to produce a fabric which could be more readily dyed than ordinary cotton.

The more modern developments of this process are dealt with under "Mercerised Cotton" (p. 114).

If cotton is treated with a concentrated solution of sodium hydroxide, to which a little carbon disulphide has been added, the fibres swell up, disintegrate and form a gelatinous mass, called "*Viscose*," which is soluble in a large volume of water, forming a viscous solution.

The formation of "viscose" is the first step in the production of a form of lustra-cellulose, or "artificial silk," known as viscose-silk, and the nature and reactions of this substance are dealt with more fully under "Artificial Silks" (see p. 115).

Experiment V., p. 88, illustrates the behaviour of cotton with dilute alkali, and the following experiment may be made to show the action of more concentrated solutions of alkali :—

Immerse a piece of cotton in a 30 per cent. solution of sodium hydroxide for about twenty minutes.

Remove the cotton, wash well, first with water then with a little dilute acetic acid, and dry.

Examine some of the fibres under the microscope, and observe that they are more cylindrical than untreated cotton fibres and that the twistings are less marked.

The Action of Other Reagents on Cotton.

Ammoniacal Copper Oxide (Cuprammonium) Solution.—For method of preparation see p. 97.

Cotton dissolves slowly in cuprammonium solution ; the process of solution being much more rapid if the cotton is previously treated with alkali.

Treat a piece of cotton wool with 30 per cent. solution of sodium hydroxide until the fibres begin to swell (see p. 111). Remove the cotton wool from the solution, wash well, first with water, then with a solution of ammonia, treat with ammoniacal copper oxide solution and boil. The cotton wool will rapidly dissolve.

A solution of cotton in ammoniacal copper oxide solution is used in the manufacture of certain varieties of artificial silk (see p. 117).

Action of Chlorine on Cotton.—Dilute solutions of chlorine

or hypochlorites have very little action on cotton at ordinary temperatures, but with more concentrated solutions at a higher temperature the fabric will be tendered, or completely disintegrated, owing to the formation of oxycellulose (see p. 109). Oxycellulose, unlike cellulose, will reduce Fehling's solution, and the formation of oxycellulose by the over-bleaching of cotton with chlorine may be demonstrated by the following experiment.

Treat a piece of cotton with chlorine water, or with a strong solution of bleaching powder acidified with acetic acid, and dry the material without washing out the bleaching agent. When dry, wash the cotton, first with water and then with a dilute solution of sodium carbonate, cover with Fehling's solution, and boil for some little time. In the presence of oxycellulose some of the Fehling's solution will be reduced, and cuprous oxide will be deposited on the fabric as a red brown stain.

The Dyeing of Cotton.

Cotton shows little affinity for colouring matters and dyes (see p. 88, IV.).

Very few natural colours are absorbed by cotton without a mordant, and this is also true of most of the acid and basic dyes obtained from coal-tar products, and sometimes referred to as "coal-tar dyes".

Certain dyes, however, more especially those derived from benzidine ($NH_2 . C_6H_4 . C_6H_4 . NH_2$), of which Congo-red is a typical example, will dye cotton "direct," i.e. without a mordant, and these are known as "*substantive dyes*".

Hygroscopic Character of Cotton.

Cotton is less hygroscopic in character than either wool or silk. Under normal conditions it will contain from 5-8 per cent. of water.

In the spinning and weaving of cotton much depends on carefully adjusting the amount of moisture retained in the fibres during the progress of these operations; this can be effected by artificially regulating the atmospheric conditions in the spinning and weaving sheds.

FABRICS MADE FROM COTTON.

Cotton, in addition to being used for ordinary woven cotton fabrics and mixed fabrics of cotton with other textile fibres, also forms the basis of several other textile materials.

Of these, the following are the most important :—

"Mercerised cotton."

"Artificial silks" or Lustra-celluloses.

"Flannelette."

Mercerised Cotton.

Cotton which has been treated with strong caustic soda solution is sometimes described as "mercerised" (see p. 112).

The term "mercerising" is, however, more correctly used as descriptive of the process whereby cotton is rendered lustrous, by subjecting it to the combined effects of the chemical action of caustic soda and the mechanical action of tension.

John Mercer, the originator of the process (see p. 112), aimed only at producing a fabric which could be more readily dyed than ordinary cotton, and the production of a lustrous fabric by a modification of the same process is a development of more recent date.

When cotton is treated in a strong solution of caustic soda, a contraction of the fibres takes place (see p. 111), but if the fibres are kept in a state of tension during such treatment, this contraction is prevented, and the fibres become lustrous in appearance. The modern process of "mercerising," therefore, depends on treating cotton (either yarn or woven fabric), stretched on rollers to keep it in a state of tension, with a strong solution of caustic soda (about 30 per cent.).

The action of the alkali is very rapid, and in a few minutes the "mercerisation" is complete. The cotton is washed thoroughly to remove the alkali, and during this process the alkali-cellulose first formed (see p. 111) is converted into hydrated cellulose ($2C_6H_{10}O_5 . H_2O$). The cotton is then dyed and finished in the usual manner.

Mercerising may be carried out in two ways :—

(*a*) The material may be held in a state of tension during the treatment with caustic alkali and the subsequent washing process.

(*b*) The tension may be applied *after* the material has been treated with alkali, but *before* the alkali has been washed

out. The essential condition is that the tension should be applied whilst the material is in the form of alkali-cellulose, and before it is converted to hydrated cellulose, otherwise no lustre effect is produced.

Properties of Mercerised Cotton.—With the exception of its increased lustre and power of absorbing dyes and colouring matters, mercerised cotton exhibits properties similar to those of ordinary cotton, and will give the typical reactions of cotton as described on page 107.

Microscopically, mercerised cotton shows in a more marked degree the features observed in the case of cotton treated with strong alkali (see p. 112).

The tension applied in the mercerising process assists in the removal of the twists and irregularities of the cotton fibre, and mercerised cotton appears as a rather smooth cylindrical fibre (see Plate II, Fig. 9).

Mercerisation is rarely so complete that fibres lose all indication of twists, but the freedom of the fibre from such twists and irregularities is a measure of the extent to which the process has been satisfactorily carried out.

The microscope is therefore a valuable aid in determining the best conditions for the process of mercerisation.

Some fibres of mercerised cotton should be examined under the microscope and compared with those of ordinary cotton.

"Lustra-Cellulose" or "Artificial Silks".

Silk is the most costly of the textile fibres, and owing to the great demand for silk fabrics of all descriptions numerous attempts have been made to produce an imitation or "artificial silk".

The processes, which have so far proved successful on a commercial scale, all have cellulose as their basis.

In addition to cotton other forms of cellulose, e.g. ramie fibre (see p. 125) and wood pulp are used for the production of lustra-celluloses.

The "mercerising" of cotton, as described above, shows that the structure of the cotton fibre can be considerably modified by action of certain chemical reagents, and in the production of "artificial silks" this idea has been further developed, and the cellulose is obtained in the form of fine structureless threads similar in outward appearance to those of silk, but of entirely different chemical composition (see p. 87).

The term "lustra-cellulose" has been adopted as descriptive of these fibres, in preference to the term "artificial silk," since this latter term would seem to imply that a fibre of chemical composition similar to that of silk had been produced by artificial means.

Silk-like fibres have also been produced from nitrogenous organic substances, e.g. gelatine and casein; such fibres resemble silk more closely in chemical composition than do the lustra-celluloses, but they have not so far been produced on a commercial scale and need not be dealt with here.

A study of the reactions of cellulose, described in the foregoing pages, shows that this substance may be brought into solution in a number of different ways.

If a solution of cellulose, prepared by one of these methods, is forced through minute holes in such a manner that the cellulose is reprecipitated from the fine streams of solution as they emerge, the substance will be obtained in the form of fine structureless threads. This in general outline is the principle on which most of the commercial processes for the production of lustra-celluloses depend.

The various processes differ chiefly in the methods employed for bringing the cellulose into solution and the reagents used for reprecipitating it in the form of threads.

The principal varieties of lustra-cellulose may be classified according to their method of production in the following manner:—

* *Chardonnet, Pyroxylin or Collodion Silk.*—The cellulose is first converted into nitro-celluloses or pyroxylins (see p. 109) and then dissolved in a mixture of alcohol and ether. The solution ("collodion," see p. 110) is forced under pressure through minute holes (about 0·01 mm. diameter) into a warm chamber, so that the solvent rapidly evaporates, leaving a fine thread of nitro-cellulose.

This thread is highly inflammable (see p. 109) and unsuitable for use in textile fabrics, but by treatment with ammonium sulphide the nitro-cellulose is "denitrated" and a fibre of "regenerated" cellulose is obtained.

The chief disadvantage of this process on a commercial scale is the cost of the solvent (alcohol and ether), but if certain precautions are taken a large proportion of this is recoverable and can be used again.

* Chardonnet process so called after its inventor Count Hilaire de Chardonnet.

The preparation of nitro-cellulose and collodion has already been discussed (see p. 109), and the experiments previously described also serve to illustrate the production of lustra-cellulose by the Chardonnet process.

Cuprammonium Silk, Pauly's Silk, "Glanzstoff".—A solution of cellulose in ammoniacal copper oxide solution (see p. 97) is forced through fine jets and the cellulose reprecipitated by the action of acetic acid.

Dissolve a piece of cotton in ammoniacal copper oxide solution as described on page 112. Pour a little of the solution into some acetic acid and observe that the cellulose is reprecipitated.

Viscose-Silk.—Cellulose is first treated with a concentrated solution of sodium hydroxide, and carbon bisulphide is then added to the alkali-cellulose (see p. 111) thus obtained. A chemical reaction takes place with the formation of a soluble thiocarbonate derivative called "viscose".

This compound appears to be formed by the interaction of one molecule of cellulose with two molecules of caustic soda and one molecule of carbon bisulphide, and the reaction may be represented by the following equation :—

$$\underset{\text{Cellulose.}}{NaOH + C_6H_9O_4 . O\boxed{H + HO}}\ \underset{\text{Carbon bisulphide.}}{\boxed{Na + S} = C = S} \rightarrow$$

$$\underset{\text{Viscose.}}{NaOH . C_6H_9O_4 . OC\begin{matrix} \diagup\!\!\!\diagup S \\ \diagdown SNa \end{matrix}}$$

The "viscose" is dissolved in water and forced through fine openings into a saturated solution of ammonium sulphate, thus forming threads of "regenerated" cellulose.

Cover a piece of absorbent cotton with a 15 per cent. solution of caustic soda and allow it to stand for about an hour.

Remove the alkali cellulose and squeeze out the excess of alkali. (The cotton should retain about three times its own weight of solution.)

As some time is required in order to complete the conversion into alkali-cellulose, the moist mass should, if possible, be set aside at this stage for two or three days in a stoppered vessel. This, however, is not absolutely essential to the success of the experiment.

Cover the alkali-cellulose with carbon bisulphide, shake vigorously in a stoppered bottle and set it aside until the mixture becomes quite yellow (2-3 hours).

Pour off any excess of carbon bisulphide, cover the yellowish mass (viscose) with water and again allow it to stand for some hours. Finally, add more water and mix thoroughly by shaking until a brown viscous solution is obtained.

Pour a few drops of the "viscose" solution into a saturated solution of ammonium sulphate and observe that the cellulose is reprecipitated.

Properties of Lustra-cellulose.—Lustra-celluloses are harsher to the touch and lack the elasticity of true silk. They are quite as lustrous in appearance; in fact, in some cases they err on the side of over-brilliance, producing a hard and scintillating effect unlike that of ordinary or wild silks.

The chief drawback to the use of lustra-celluloses for textile fabrics is their behaviour with water; when treated with water the fibres swell and their tensile strength decreases.

For this reason fabrics made of lustra-celluloses need careful handling in the laundry and also during the process of dyeing.

Under the microscope lustra-celluloses appear as rounded structureless fibres somewhat similar to those of silk, but thicker and more regular in outline. (See Plate II, Fig. 10.)

Fibres of silk and lustra-cellulose should be mounted on the same slide, as in this manner the differences can be more readily detected. (See Plate II, Fig. 11.)

The appearance of lustra-cellulose under polarised light also differs from that of silk; this difference may be rendered more apparent by mounting the fibres in a drop of aniline.

If the Nicol's prism* is slowly rotated it will be observed that there is one position in which silk fibres become almost invisible, namely, when the longitudinal axis of the fibre is at right angles to the plane of polarisation* and that maximum visibility is obtained when the Nicol is at right angles to this position.

With fibres of lustra-cellulose, on the other hand, colour changes are observed on rotating the Nicol, but the fibres are distinctly visible in all positions.

Reactions of Lustra-celluloses.—Lustra-celluloses, it should be remembered, are of vegetable origin and are composed almost entirely of cellulose; their chemical composition is,

* For the meaning of the terms "Nicol's prism" and "Plane of Polarisation," see "Polarisation of Light," Vol. II.

therefore, quite different from that of real silk, which is of animal origin and contains amino groups.

The reactions previously described for differentiating animal and vegetable fibres may, therefore, be used to distinguish between real and artificial silks. (See pp. 87-89, "Reactions of Animal and Vegetable Fibres".)

The burning tests (I. and II.) and also the Xanthoproteic reaction (III.) are of especial importance. Lustra-celluloses swell and become gelatinous on treatment with alkali, but do not dissolve (see V.). The difference in behaviour with colouring matters (IV.) is not so marked, since lustra-celluloses, like mercerised cotton, absorb dyes more readily than ordinary cotton.

Ammoniacal copper oxide solution (see p. 97) dissolves both silk (fibroin) and lustra-celluloses, but in the latter case a white precipitate of cellulose is obtained on diluting the solution with water.

An alkaline solution of copper oxide containing glycerine will, however, dissolve silk, but has no action on lustra-celluloses. This reagent may be used for the quantitative separation of silk and lustra-cellulose (see p. 133).

Compare the action of ammoniacal copper oxide solution on specimens of silk and lustra-cellulose. Dilute the solutions obtained with water. In the case of lustra-cellulose the cellulose separates out as a white precipitate.

Immerse threads of silk and lustra-cellulose in alkaline copper glycerine solution (see p. 98) and observe that, after standing for some time at the room temperature, the silk dissolves and the lustra-cellulose remains unchanged.

Various methods have been suggested for distinguishing the different varieties of lustra-cellulose from one another; these mostly depend on colour reactions and are in some cases only applicable to unbleached fibres.

Collodion "silks" usually contain traces of nitrocelluloses, though the amount of nitrogen present is extremely small, about 0·2 per cent.

The other lustra-celluloses do not contain any nitrogen, and "collodion silk" may be distinguished from the other forms of lustra-cellulose by treating with concentrated sulphuric acid to which a trace of diphenylamine has been added.

Collodion silks give a bright blue colour and the other lustra-celluloses only a slight yellow colour.

"Flannelette."

Flannelette is a fabric produced by weaving cotton in such a manner that a material somewhat similar in texture and outward appearance to a woollen fabric is obtained.

Cotton woven in the ordinary manner gives a fabric with a smooth surface, and if suitably "dressed" it readily takes a polish on ironing; whereas in the case of flannelette the fabric is so treated that minute threads of cotton project from the surface of the material. This gives it a rough appearance, and at the same time ensures the formation of a non-conducting layer of air between the material and the surface with which it is in contact. In this manner the non-conducting properties of a woollen fabric are to some extent reproduced.

Flannelette is, in fact, a cotton fabric which has been subjected to a special mechanical process, and the fibres of which it is composed will show all the chemical and microscopical properties of ordinary cotton.

Some fibres from a piece of flannelette should be examined under the microscope and identified as cotton fibres. (See Plate I, Fig. 4.)

Owing to the nature of its surface, flannelette is more inflammable than ordinary cotton, and this has proved a serious drawback to its use as a textile material.

It was observed (see p. 100) that "weighted" silks burn less readily than untreated silks, and in the same way if flannelette or other cotton fabric is loaded with mineral matter the material is rendered less inflammable.

Numerous processes have been devised for "fire-proofing" flannelette by loading it with various mineral substances. The substances which may be used for this purpose vary greatly in character, and among those most frequently employed are the following: ammonium salts (phosphate, sulphate, carbonate); magnesium chloride and sulphate; aluminium salts (alum, aluminium sulphate); silicates; borates; sodium tungstate and sodium stannate.

The nature of the fire-proofing materials added to flannelette is usually determined by making a complete analysis of the ash, i.e. the residue obtained after the removal of all the organic matter by burning, and is a rather complex process. Some idea of the nature of the substances can, however, be obtained by making the following experiments:—

Burn a small piece of flannelette in a Bunsen flame; if the cotton burns away, leaving an ash which retains the original structure of the fabric, the material has been "dressed" with mineral matter, probably for the purpose of fire-proofing (see p. 100).

If the above test indicates that the material has been "fire-proofed" some of the flannelette should be cut into strips and ashed in the manner described for silk (see p. 104).

Extract the ash with hot water, filter and wash the residue with hot water.

Examine the filtrate for soluble salts, e.g. chloride, sulphate, borate, and for magnesium.

Extract the residue insoluble in water with hydrochloric acid, and again filter.

Examine the filtrate for tin, silicate, and also for tungsten. The test for tungsten is made as follows:—

To the hydrochloric acid solution add a few pieces of zinc. In the presence of tungstates a blue colour develops on standing, owing to the formation of oxides of tungsten (tungsten tungstate, W_3O_8 or $2WO_3 . WO_2$).

If any considerable residue is obtained after extraction with hydrochloric acid it should be fused with fusion mixture and potassium nitrate, and the fused mass examined in the usual manner for silicate, tin, alumina, etc. (see p. 105).

The efficacy of the "fire-proofing" process depends to a great extent on the insolubility in water of the mineral salts added, since on washing the fabric in the ordinary manner with soap and water, the soluble salts will be dissolved out.

For this reason a determination of the proportion of soluble matter in the ash is, from the practical point of view, of more importance than a determination of the exact nature and quantity of the various mineral salts added.

This determination can be carried out in the following manner:—

** *Determination of Soluble Matter in the Ash of "Flannelette".*—Weigh out a piece of flannelette (about 2 gms.), ash and determine the weight of the ash as described above (see p. 104).

Transfer the ash to a beaker, cover with distilled water and boil for about ten minutes.

Pour off the water through a filter, add more water to the ash and again boil and filter. Finally, transfer the ash to the filter, wash several times with hot water, dry, ignite and weigh.

The difference between this weight and that of the total ash gives the weight of soluble matter present.

The above experiment gives the proportion of soluble matter present in the "dressing," after ignition,* but this does not necessarily represent the total amount of mineral matter removed from the fabric during the ordinary process of washing, since a considerable amount of the insoluble matter may be "washed out" of the fabric together with the adhering dirt.

This may be shown by making the following experiment :—

Weigh out two pieces of flannelette (each about 5 gms.).

(*a*) Determine the percentage of ash (mineral matter) in one piece, as described above.

(*b*) Immerse the other piece in an aqueous soap solution containing about 0·5 per cent. of soap, and heat. Stir and turn the material at intervals with a glass rod, and allow the solution to boil briskly for about ten minutes.

Remove the fabric from the solution, rinse *well* with water, dry and determine, by ashing, the percentage of mineral matter left in the fabric.

It is essential that the soap should be removed from the fabric as completely as possible by rinsing, since any soap left in the fabric will be converted to carbonate on ignition, and will increase the amount of mineral matter found in the fabric.

The percentage ash obtained for (*b*) is usually considerably less than that in (*a*), the difference showing what proportion of the mineral matter has been removed.

In the case of one specimen examined 90 per cent. of the mineral matter was removed by this treatment.

Thus loading with mineral matter can hardly be considered a satisfactory method of permanently reducing the inflammability of flannelette, which has to be washed frequently. To be effective, the fire-proofing process should really be repeated after each washing, or at least at short intervals.

Linen.

Linen is a fibre obtained from the inner bark or bast fibres of the flax plant.

The flax plant, when fully grown, is cut down or pulled up by the roots ; the seeds and leaves are then separated from the stalks by a mechanical process technically known as "rippling".

* On ignition some of the soluble matter may be rendered insoluble.

The stalks are tied in bundles and exposed to the action of water and air for several days. This process is described as "retting" (or rotting), as under these conditions the woody tissues of the plant are broken down by fermentation, and the inner fibrous cellulose can then be separated from the decomposed tissues by a series of mechanical operations.

"Retting" may be carried out either by placing the flax in stagnant water, "pool-retting," or by exposing it to the action of running water in a stream.

The Courtrai flax of Belgium is "retted" in the river Lys, and flax "retted" in this manner is usually a better colour than "pool-retted" flax.

Flax may also be "retted" by exposing it to the action of dew and sun, "dew-retting," but the method gives uneven results, the fibres obtained are rather dark in colour, and are usually considered inferior to those obtained by other processes of "retting".

Attempts have also been made to bring about the "retting" of flax with specially prepared bacterial cultures.

Linen fibres are more lustrous and considerably longer than those of cotton, and their tensile strength is greater. They are, however, more readily disintegrated (see p. 124) and "over-retting" makes the fibres brittle.

Microscopical Appearance.

Under the microscope the fibres are seen to be composed of bundles of cylindrical cells, which show fine longitudinal markings, and occasional transverse markings and knot-like joints (resembling the knots in straw). (See Plate II, Fig 12.)

The lumen shows as a narrow streak or line in the centre of the fibres, and the fibres taper to a point at the ends.

In cross-section the fibre is polygonal and shows a small round lumen.

Examine some fibres of linen under the microscope, then moisten the fibres with dilute iodine solution (see p. 126), and examine again. The treatment with iodine renders the characteristic markings more apparent.

In examining fibres from a piece of linen fabric, any starch added as dressing must be removed before staining the fibres with iodine.

Chemical Properties of Linen.

Flax fibres are composed almost entirely of cellulose (about 90 per cent.), the other substances present being water (6-8 per cent.), and small quantities of fat, wax and pectose.

By suitable chemical treatment, flax may be made to yield a pure cellulose, chemically indistinguishable from cotton cellulose.

The chemical reactions of linen are, therefore, essentially the same as those of cotton, and differ only in one or two minor respects.

The following differences should be noted :—

Action of Sulphuric Acid.—Linen is less readily attacked than cotton by the action of concentrated sulphuric acid, and this may be used as a distinguishing test.

Immerse fibres of cotton and linen in concentrated sulphuric acid for two minutes, wash well with water, and then with water containing a little ammonia, and dry.

Cotton fibres form a gelatinous mass soluble in water.

Linen fibres are comparatively little affected.

Any dressing in the fibres should be removed before applying the tests, by boiling with distilled water for a few minutes, and gently rubbing.

Action of Ammoniacal Copper Oxide (Cuprammonium) Solution.—Linen swells upon treatment with ammoniacal copper oxide, but does not dissolve (see p. 112).

Action of Oxidising Agents.—Owing to its structure linen is more easily disintegrated than cotton by the action of bleaching powder and other oxidising agents, and also by boiling solutions of alkali in the presence of air (see p. 111).

Moisten some linen fibres arranged on a microscope slide with a drop of dilute chromic acid solution. Allow to stand for a few minutes, cover with a cover-slip, and examine under the microscope.

The linen fibres are broken down into their constituent cells by the action of the chromic acid. Cotton fibres being unicellular are not so readily disintegrated.

The Dyeing of Linen.

Linen is even less reactive than cotton with dyes, and this is sometimes made use of in distinguishing tests. Such tests are, however, only reliable when the linen is unbleached; bleached linen shows little or no difference from cotton.

Hygroscopic Character.

Linen under normal conditions contains about the same percentage of moisture as cotton, i.e. 7-8 per cent. (see p. 113).

OTHER BAST FIBRES, RAMIE, JUTE AND HEMP.

These fibres are all somewhat similar in nature to flax fibres, but are not used very extensively in the production of textile fabrics, so that only a brief description of their properties need be given here.

Ramie or China Grass is a bast fibre of a plant of the nettle family; it is strong and durable and probably ranks first of the vegetable fibres in these respects. It is more lustrous than linen, but is rather harsh and inelastic.

The decortication of the fibre from the plant is somewhat difficult and has to be done by hand. This has, so far, prevented a more extensive use of the fibre for textile purposes.

The fabrics described as "Grass-Lawn" and "Indian Lawn," if genuine, are composed of ramie.

Chemical Composition.—Ramie is composed almost entirely of cellulose; but certain varieties appear to contain some lignocellulose, since they give a slight yellow coloration with aniline sulphate (see p. 126).

Microscopical Appearance of Ramie.—The bast cells are considerably larger than those of linen, and both the lumen and the fibre itself show considerable variation in width. The cross-section is elliptical.

Jute is a fine, lustrous fibre, but lacks strength and durability, and rapidly deteriorates if exposed to action of moisture. For this reason its use is confined chiefly to the production of coarse woven fabrics, e.g. sacking, etc.; but it is also used in certain forms of tapestry and as a binding thread in the weaving of carpets.

Chemical Composition.—Jute differs in chemical composition from linen, since it consists essentially of a compound of cellulose known as *ligno-cellulose*, and jute is sometimes described as a "*lignified fibre*" (see p. 126).

Microscopical Appearance.—Jute fibres are rather smooth in appearance and transverse markings are absent. The lumen varies in width and the cross-section is polygonal, showing an oval lumen.

Hemp is a harsh, stiff fibre of considerable tensile strength and durability, and in these respects differs very markedly from jute. It is used chiefly in the production of twine, cord, etc.

Chemical Composition.—Hemp is composed partly of cellulose and partly of ligno-cellulose (see below).

Microscopical Appearance.—Under the microscope, hemp is very similar in appearance to flax. The ends of the fibres are usually blunt and sometimes forked; this forking is not shown by linen fibres. In cross-section the fibres are elliptical, and this is also a means of distinguishing them from linen (see p. 123).

Colour Reactions of Unbleached "Ligno-Cellulose".

Ligno-cellulose reacts with various aromatic compounds, giving coloured derivatives, and these reactions are made use of in testing for "lignified fibres". Lignified fibres which have been bleached by the action of chlorine, sulphur dioxide, etc., *do not* give these colour reactions, and such tests are therefore limited to the examination of unbleached fibres.

Aniline Sulphate.—Immerse the fibres in an aqueous solution of aniline sulphate (about 1 per cent.). The fibres are stained yellow or orange.

Phloroglucinol.—Immerse the fibres in an alcoholic solution of phloroglucinol (5 per cent.), dry, and then expose them to the action of hydrochloric acid gas.

This may be done by warming a little concentrated hydrochloric acid in a dish and holding the fibres in the fumes.

The fibres are stained a bright red colour.

If fibres of unbleached jute or hemp are not available the colour reactions with aniline sulphate and phloroglucinol can be shown with a piece of ordinary newspaper.* This paper is usually prepared from wood pulp and contains ligno-cellulose. The paper should be moistened with a few drops of the reagent and not immersed in the solution.

Iodine and Sulphuric Acid.—Lignified fibres treated with a dilute solution of iodine and then with sulphuric acid are stained yellow; fibres of cellulose are stained blue.

Hemp which is composed partly of cellulose and partly of ligno-cellulose gives a greenish colour.

This is also a convenient method of staining bast fibres which are to be examined with the microscope (see p. 123).

* Newspaper usually contains some unbleached fibres.

The solutions required may be prepared as follows :—

(*a*) Dissolve 3 gms. of potassium iodide in 60 c.c. of water and add 1 gm. of iodine. Dilute the solution 1 : 10 before using.

(*b*) Dilute 3 parts of concentrated sulphuric acid with 1 part of water, and, if required for microscopic work, add 1 part of glycerol ; this prevents the destruction of the fibres by the acid and brings out certain differences in structure.

Quantitative Examination of Mixed Fabrics.

A careful study of the chemical reactions of the textile fibres, as described in the foregoing pages, indicates that it should be possible, by a suitable selection of reagents, to make a quantitative separation of the principal textile fibres (wool, silk and cotton) present in fabrics composed of mixtures of these fibres. It will also be seen that in some cases there is a considerable choice of reagents available for this purpose.

The following experiments are selected to show how such separations may be carried out, and to illustrate some of the methods which have been found to give good results in practice.

For further information of this subject see "Textile Fibres" (Matthews).

Preliminary Examination with the Microscope.

Before making any quantitative separation of a mixed fabric, some of the "*warp*" and some of the "*weft*" threads should be carefully examined under the microscope ; this will show which fibres are present, and the separation can then be made accordingly.

The threads running the length of the cloth are called the "*warp threads*" or "*ends*". Those that intersect or run across the warp threads are called "*woof*," "*weft*" or "*filling*" threads. The "filling" threads which bind in the warp threads at either side form the *selvage.*

Weighing of Fabrics.

For carrying out quantitative determinations, fabrics may either be weighed in the air-dry condition, or they may be dried at 100° C. and weighed in a stoppered vessel.

The condition in which the fabric is weighed should be stated, i.e. "air-dry" or dried at 100° C.

In the experiments here described the fabrics, unless otherwise stated, are weighed in the air-dry condition.

(For precautions to be taken in restoring the material to the air-dry condition after drying see p. 94.)

SEPARATION OF WOOL AND COTTON.

In fabrics containing only two different kinds of fibre the quantities of two constituents present are usually determined in the following manner :—

(1) The total amount of fibre (i.e. the weight of fabric after the removal of finishing materials or dressing) is determined.

(2) The amount of one of the constituents is determined by direct experiment.

(3) The amount of the second constituent is obtained as the difference between (1) and (2).

In the case of wool and cotton it is possible, however, by making two experiments, to determine the quantity of both constituents *directly*, and this method is therefore recommended, since it is more instructive and a check on the accuracy of working is obtained.

Determination of Wool.

(*a*) Cotton is soluble in a concentrated solution of sulphuric acid ; wool is very little affected by this reagent, and a separation of wool from cotton can be made in the following manner :—

Immerse a weighed piece of the fabric (2-5 gms.) in 80 per cent. sulphuric acid for twelve hours. Wash the residue, first with a mixture of equal parts of alcohol and water and then with alcohol to ensure the complete removal of the cotton. Dry the residue, restore to the air-dry condition and weigh.

If the residue becomes disintegrated and cannot be washed and dried in one piece, it should be collected and dried on a filter paper, restored to the air-dry condition and weighed.

(*b*) If wool fibres are present both in the warp and in the weft threads (this will be indicated in the preliminary microscopical examination) the following method can also be used for separating cotton from wool, and has been found in practice to give more satisfactory results than method (*a*).

Dilute acids have very little action on wool, whereas cotton, if treated with dilute acids and dried without washing, is tendered and rendered brittle (see p. 107). A separation can therefore be effected in the following manner :—

Immerse a weighed piece of the fabric (2-5 gms.) in dilute

hydrochloric acid (1 part of concentrated acid to 8 parts water) for about fifteen minutes. Remove the material from the solution, and *without washing* it, dry as rapidly as possible, preferably in front of a fire. The cotton darkens and becomes brittle and can be completely removed from the material by gently rubbing and shaking. The wool is restored to the air-dry condition and weighed.

Care should be taken not to rub too hard, or particles of wool are liable to become detached.

The wool fabric should appear uniform in texture when held against the light; dark irregular patches indicate that the cotton has been incompletely removed.

A photograph of the wool fabric separated from a cotton and wool fabric in this manner is shown in Fig. 8, B.

Determination of Cotton.

Wool is soluble in a 5 per cent. solution of potassium hydroxide, whereas cotton is little affected by this reagent except on prolonged boiling (see p. 111).

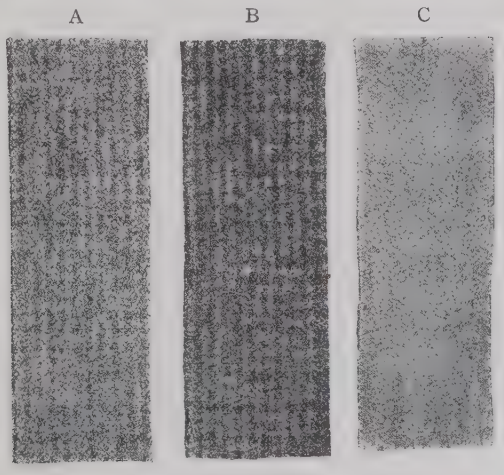


FIG. 8.—Separation of wool and cotton fabric. A—wool and cotton fabric. B—wool fabric separated from A. C—cotton fabric separated from A.

Cotton may therefore be separated from wool in the following manner:—

Weigh out a piece of the material (2-5 gms.) and boil it

for about fifteen minutes in a 5 per cent. solution of caustic potash.*

Remove the material from the solution and wash thoroughly, first with water containing a little acetic acid and then with water. Dry, restore to the air-dry condition and weigh.

The weight of cotton in the material is thus obtained; but since cotton loses from 3-5 per cent. of its weight on boiling with caustic potash, it is usual, on this account, to add to the cotton 5 per cent. of its weight. A photograph of the cotton fabric separated from a wool and cotton fabric in this manner is shown in Fig. 8, C.

The following example shows the method of calculation :—

Determination of Wool and Cotton in a Mixed Fabric.

Determination of Wool.—

Weight of sample (air-dry) = 2·15 gms.

Weight of wool (air-dry) obtained from sample = 1·10 gm.

$$\text{Therefore percentage of wool} = \frac{1{\cdot}10}{2{\cdot}15} \times 100 = \underline{51{\cdot}1}.$$

Determination of Cotton.—

Weight of sample (air-dry) = 2·20 gms.

Weight of cotton obtained from sample = 0·98 gm.

$$\text{Add 5 per cent. correction} \left(= 0{\cdot}98 \times \frac{5}{100} \right) = 0{\cdot}05 \text{ gm.}$$

Corrected weight of cotton = 1·03 gm.

$$\text{Percentage of cotton} = \frac{1{\cdot}03}{2{\cdot}2} \times 100 = \underline{46{\cdot}9}.$$

Total fibre (air-dry) present in fabric = wool + cotton

= 46·9 + 51·1 = 98·0 per cent.

The above experiments, if carefully carried out, should give with a fair degree of accuracy the proportions of wool and cotton present in a mixed fabric. Since in preparing mixed fabrics the fibres are not specially dried, but are used in the air-dry condition, it is more satisfactory, from the practical point of view, to make the determinations on air-dry materials as described above.

If more accurate results are required, the amount of finishing materials and also the moisture present in the fabric

* *Caustic soda*, it is stated (Matthews), does not give such satisfactory results, but owing to the high price of caustic potash it may at the present time be used.

should be determined by direct experiment, and the separated cotton and wool should be dried at 100° C. to a constant weight. For further details of procedure see "Textile Fibres" (Matthews).

SEPARATION OF SILK AND WOOL.

Silk is more reactive towards chemical reagents than any of the other fibres, and it is therefore possible to dissolve out the silk from mixtures of silk with either wool, or cotton, or both (see below); but so far no method has been devised by which the wool can be removed and the silk left unaffected. In the case of wool and silk mixtures, therefore, the method outlined on page 128 must be employed.

(a) Determination of Finishing Materials or "Dressing".

Weigh out a piece of the fabric (2-5 gms.) and boil first in a 1 per cent. solution of hydrochloric acid for fifteen minutes, and then in a 0·05 per cent. solution (N/100) of sodium carbonate for the same time. Wash well with water and weigh when restored to the air-dry condition. This gives the total amount of fibre present in the material.

(b) Determination of Wool.

Silk is rapidly dissolved by concentrated hydrochloric acid in the cold,* whereas wool is not affected to any marked extent by this reagent. A quantitative separation of the two fibres can thus be made in the following manner:—

Immerse the fabric after the removal of the dressing, as described above, in concentrated hydrochloric acid for about five minutes. Wash thoroughly, restore to the air-dry condition and weigh.

This gives the weight of wool present in the fabric.

The total amount of fibre (*a*), less the amount of wool (*b*), gives the amount of silk.

As an alternative method the silk may be dissolved out by the action of a solution of basic zinc chloride. (See Separation of Silk, Wool and Cotton, p. 132.) Care must be taken to wash out the zinc salt completely, and, for this reason, the fabric should be rinsed in water containing a little acetic acid.

* This is only true if the silk is free from weighting (see p. 100).

A photograph showing the separation of a silk and wool fabric is shown in Fig. 9. In this case the warp threads were

FIG. 9.—Separation of a wool and silk fabric. A—wool and silk fabric. B—strands of wool separated from A.

composed of wool and the weft threads of silk, so that a complete wool fabric could not be separated.

SEPARATION OF SILK AND COTTON.

The methods given for separating silk from wool may also be used for separating silk from cotton.

If a concentrated solution of hydrochloric acid is used, however, special care must be taken to remove all the acid from the material before drying (see p. 107), and the cotton should be washed first with water containing a little alkali, and then with water alone. It is usual also to apply a correction of 4 per cent. to the weight of cotton obtained, to compensate for loss undergone during the treatment (cf. p. 130).

Silk may also be separated from cotton by the action of alkaline copper-glycerine solution. (See Separation of Silk from Lustra-cellulose, p. 133.)

SEPARATION OF SILK, WOOL AND COTTON.

The following method may be conveniently employed :—

The dressing or finishing materials are removed from the

fabric, and the total amount of fibre present determined (see p. 131). Let this weight = (*a*).

The silk is then removed by immersing the fabric in a boiling solution of basic zinc chloride (see p. 97) for two minutes. The fabric is well washed first with water containing a little acid, and then with water alone. The residual cotton and wool are then restored to the air-dry condition and weighed. Let this weight = (*b*).

The wool and cotton are then separated by treatment with 5 per cent. caustic potash (see p. 129).

The residual cotton is washed, restored to the air-dried condition, and weighed. Let this weight = (*c*).

(A correction of 5 per cent. is added to the cotton after this treatment, see p. 130.)

Then $(a - b)$ = weight of silk.

$b - (c + 5$ per cent. of $c)$ = weight of wool.

$c + 5$ per cent. of c = weight of cotton.

SEPARATION OF SILK AND LUSTRA-CELLULOSE.

Real silk is soluble in an alkaline solution of copper oxide containing glycerine (see p. 98), whereas lustra-celluloses do not dissolve in this reagent.

The total amount of fibre in the material should first be determined (see p. 131). The silk can then be dissolved out by immersing the fabric for thirty minutes in alkaline copper-glycerine solution *at the room temperature* (see p. 119). The residual lustra-cellulose is then carefully washed, dried, restored to the air-dry condition, and weighed.

Chapter V.

BLEACHING AGENTS.

Chemical reagents which are used for the removal of colouring matters from textiles are usually described as "*bleaching agents*". Bleaching agents may be used to remove the natural colouring matter of fibres, to remove a dye, or to take out a stain. The colouring matters which have to be dealt with are, with one or two exceptions (e.g. iron compounds*) organic substances, and bleaching, as ordinarily understood, consists in the conversion of coloured organic compounds into colourless derivatives.

There are two general methods by which bleaching may be effected :—

(1) By the *oxidation* of the colouring matter to a colourless derivative.

(2) By the *reduction* of the colouring matter to a colourless derivative.

I. Bleaching by Oxidation.

This may be accomplished by the action of the oxygen of the air, or by oxidising agents, i.e. substances which give up oxygen (peroxides, etc.), or which liberate oxygen from other substances (chlorine, etc.). The agencies most commonly made use of for bleaching by oxidation are the following :—

Light and air.

Chlorinated lime ("bleaching powder") and hypochlorites.

Peroxides : hydrogen peroxide, sodium peroxide.

Persalts : sodium perborate.

Potassium permanganate (in conjunction with other reagents).

* Stains produced by iron compounds, e.g. Fe_2O_3, are usually removed by dissolving out the iron with an acid (see p. 162), and this process hardly comes within the category of bleaching.

LIGHT AND AIR.

Most colouring matters are bleached on prolonged exposure to light and air, and bleaching can be effected in this manner with the least possible deterioration of the fabric. The process is, however, in many cases, extremely slow, and it is often necessary to resort to some more rapid method of bleaching.

CHLORINATED LIME (BLEACHING POWDER) AND HYPOCHLORITES.

One of the reagents most frequently used for bleaching textiles is the substance known as "chlorinated lime" or bleaching powder.

Bleaching powder is prepared by passing chlorine gas over slaked lime, and its formation can be represented by the following equation :—

$$Ca\begin{cases}OH\\OH\end{cases} + Cl_2 \rightarrow Ca\begin{cases}OCl\\Cl\end{cases} + H_2O$$

Slaked lime. Bleaching powder.

Bleaching powder may be regarded as a mixed salt of hydrochloric and hypochlorous acid thus :—

$$Ca\begin{cases}H\,Cl\\O + H\,OCl\end{cases} \rightarrow Ca\begin{cases}Cl\\OCl\end{cases} + H_2O.$$

On treatment with dilute acids this substance gives off chlorine :—

$$Ca(OCl)Cl + HCl \rightarrow CaCl_2 + HOCl$$
$$HOCl + HCl \rightarrow H_2O + Cl_2.$$

In the presence of oxidisable colouring matter and water, the chlorine will react with the water, liberating oxygen, and the colouring matter is thus oxidised or bleached.

$$Cl_2 + H_2O \rightarrow 2HCl + O.$$

It should be noted that the oxygen is liberated in the fabric in the "nascent" state, and in this condition has much more powerful bleaching properties than ordinary molecular oxygen.

The active agent in bleaching powder is the chlorine liberated by the action of dilute acid, and this is usually termed the "*available chlorine*".

It is possible to prepare bleaching powder containing up to 43 per cent. of available chlorine, but commercial preparations usually contain about 30-36 per cent. of available chlorine, and in addition contain some free lime (i.e. lime not combined with chlorine).

On keeping, bleaching powder tends to decompose with the formation of calcium chloride and chlorate, and on exposure to air and moisture the carbon dioxide of the atmosphere causes a partial liberation of the chlorine :—

$$6Ca(OCl)Cl \rightarrow 5CaCl_2 + \underset{\text{calcium chlorate.}}{Ca(ClO_3)_2}$$

$$2Ca(OCl)Cl + H_2CO_3 \rightarrow CaCO_3 + CaCl_2 + 2HClO.$$

The hypochlorous acid first produced decomposes with the liberation of chlorine.

Hence the amount of available chlorine in different samples of bleaching powder may vary considerably, but the amount actually present can readily be determined in the following manner :—

Determination of Available Chlorine in Bleaching Powder.

If potassium iodide be added to a solution of bleaching powder and the mixture acidified, the chlorine liberated reacts with the iodide, setting free an equivalent quantity of iodine.

$$\underset{2 \times 35{\cdot}5}{Cl_2} + 2KI \rightarrow 2KCl + \underset{2 \times 127}{I_2}.$$

The amount of iodine thus liberated can be determined by titration with a decinormal solution of sodium thiosulphate.

$$\underset{2 \times 248}{2Na_2S_2O_3 . 5H_2O} + \underset{2 \times 127}{I_2} \rightarrow 2NaI + Na_2S_4O_6 + 5H_2O.$$

The method of procedure is as follows :—

Weigh out 10 gms. of bleaching powder, using a weighing bottle, into a porcelain mortar. Add about 5 c.c. of water and mix thoroughly until a smooth paste is obtained.

Gradually dilute the paste with more water, stir well and pour off the milky fluid into a litre flask.

Rub down the residue left in the mortar with a little more water, and again pour off the liquid into the litre flask.

Repeat this process until all the powder has been transferred to the flask, then make up the volume to 1000 c.c. and shake well.

Measure out 25 c.c. of the solution with a pipette into a conical flask, add 5 c.c. of a 10 per cent. solution of potassium iodide and acidify with dilute acetic acid.

Iodine is liberated and the solution turns brown.

Run in decinormal sodium thiosulphate solution from a burette, until the solution turns from brown to pale yellow, then add two or three drops of clear, freshly prepared starch solution (see p. 16) and continue to run in the sodium thiosulphate solution until the blue colour, at first obtained, just disappears.

At this stage more acetic acid should be added; if all the available chlorine has been liberated no change in colour will be observed, but if more chlorine, and therefore more iodine, is set free, the starch will again turn blue and the titration must be continued until the reaction is complete.

The above equations show that 248 parts $Na_2S_2O_3 . 5H_2O$ are equivalent to 127 parts iodine, and 127 parts iodine are equivalent to 35·5 parts chlorine.

A decinormal solution of sodium thiosulphate contains 24·8 gms. of crystalline thiosulphate ($Na_2S_2O_3 . 5H_2O$) in 1 litre.

Therefore 1 c.c. N/10 sodium thiosulphate = 0·0248 gm. thiosulphate.

Or 1 c.c. N/10 sodium thiosulphate = 0·0127 gm. iodine.

" " " " = 0·00355 gm. chlorine.

Hence the "available chlorine" present in 25 c.c. of the bleaching powder solution is obtained by multiplying the number of c.c. of N/10 thiosulphate used by 0·00355.

Or the "available chlorine" present in 1 litre of solution (10 gms. powder) = c.c. of N/10 thiosulphate × 0·00355 × 40.

This result multiplied by 10 gives the percentage of available chlorine in the powder.

Alkaline Hypochlorites.

Solutions of sodium or potassium hypochlorite are sometimes used as a source of chlorine for bleaching purposes, in preference to bleaching powder. The absence of calcium compounds in such preparations is considered an advantage, since the possible formation of insoluble calcium soaps in the subsequent washing process is thus avoided.

On acidifying the solution of hypochlorite with dilute acid, chlorine is liberated.

$$NaOCl + 2HCl \rightarrow NaCl + H_2O + Cl_2.$$

A solution of sodium hypochlorite can be prepared by passing chlorine into a solution of caustic soda in the cold * or by the electrolysis of a solution of common salt.

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O.$$

Such a solution is sometimes sold under the name of "Javel water" or "Eau de Javel," though originally this product appears to have contained potassium hypochlorite (KOCl).

A solution of sodium hypochlorite can also be obtained by adding excess of sodium carbonate to a solution of bleaching powder.

$$Ca(OCl)Cl + Na_2CO_3 \rightarrow CaCO_3 + NaCl + NaOCl.$$

The insoluble calcium carbonate is allowed to settle, and the clear liquid containing the hypochlorite is decanted and used.

"*Available Chlorine*" *in a Solution of Hypochlorite.*—The amount of available chlorine in a solution of hypochlorite can be determined by acidifying a measured volume of the solution with acetic acid, in the presence of excess of potassium iodide, and determining the amount of iodine thus liberated with decinormal sodium thiosulphate solution as described under Bleaching Powder (p. 136).

The Use of Chlorine as a Bleaching Agent.

Chlorine, in the form of either lime or soda compound, should not be used for bleaching silk or woollen fabrics, the fibres of which are attacked by chlorine and rendered harsh and brittle (see pp. 92 and 97).

The use of chlorine should be restricted to the bleaching of linen and cotton, i.e. cellulose; and even cellulose, it should be remembered, is by no means unaffected by the action of chlorine (see pp. 112 and 124).

It is therefore necessary to exercise considerable care in using chlorine as a bleaching agent. The directions given below indicate the maximum strength of solution which ex-

* If chlorine is passed into a warm solution of caustic soda, chlorate and chloride are obtained.

$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O.$$

perience has shown it is reasonably safe to adopt, and the precautions which should be taken to avoid damage to the fabric.

Preparation of a Solution of Chlorine for Bleaching.—A solution of chlorine used for bleaching textiles should not contain more than about 0·15-0·2 per cent. of "available chlorine".

Since bleaching powder contains about a third of its own weight of available chlorine, a solution prepared by mixing 6 gms. of bleaching powder with 1 litre of water will contain about 2 gms. of available chlorine per litre, or 0·2 per cent. of "available chlorine".

The solution should be allowed to settle and the clear liquid only should be used.

If the fabric is immersed in the turbid solution over-bleaching may occur in places, also any insoluble calcium compounds present will tend to settle on the fabric, and form insoluble calcium soaps during the subsequent process of washing with soap and water (see p. 18).

Sodium Hypochlorite Solution.—A solution of sodium hypochlorite, containing about 0·2 per cent. of available chlorine, can be prepared by mixing 6 gms. of bleaching powder with 600 c.c. water and adding to it 8 gms. of sodium carbonate (anhydrous) dissolved in 400 c.c. water. The mixture should be well stirred, allowed to settle and the clear liquid poured off and used.

In working with large quantities it is often more convenient to measure in ounces and gallons.

One gallon of water = 10 lb.

Therefore a solution obtained by mixing 6 lb. of bleaching powder with 100 gallons of water (1000 lb.) will be of the same strength as that described above, and will contain about 0·2 per cent. of "available chlorine".

One gallon of this solution will contain 0·06 lb. of bleaching powder

= 0·06 × 16 ozs. bleaching powder
= 0·96 oz. bleaching powder
= 1 oz. (approximately).

Hence a solution prepared by mixing 1 *oz.* of bleaching powder with 1 *gallon* of water will be of convenient strength for bleaching purposes.

The article to be bleached should be steeped in the bleaching powder or hypochlorite solution for a few minutes, and

then transferred, without rinsing, to a bath containing a 2·5 per cent. solution of glacial acetic acid.

A solution of sulphuric acid containing not more than 0·8 per cent. of pure acid may be used (sp. gr. 1·005), but the solution of acetic acid is in all cases to be preferred, as under these conditions the bleaching is effected chiefly by the action of hypochlorous acid, and the only free acid left in the fabric is acetic acid.

The reactions of bleaching powder with acetic acid can be represented by the following equations :—

$$Ca(OCl)Cl + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + HOCl + HCl$$

$$HOCl \rightarrow HCl + O$$

$$(CH_3COO)_2Ca + 2HCl \rightarrow 2CH_3COOH + CaCl_2.$$

In the case of sulphuric acid, chlorine is liberated and any excess of sulphuric acid is left in the fabric.

$$Ca(OCl)Cl + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2.$$

Very complete rinsing is therefore necessary if sulphuric acid is used, and it is advisable to add a little alkali to the last rinsing but one, or to wash the fabric thoroughly with soap and water in order to ensure that no free acid is left in it; since however dilute the solution may be, the acid becomes concentrated on drying, with the result that the fabric is tendered. This is more particularly the case if the fabric is dried rapidly by ironing with a hot iron (see p. 107).

By using acetic acid this difficulty is to a great extent obviated, as traces of this acid left in the fabric have little or no effect on the fibres even on drying (see p. 110).

If the colour is not completely removed by the action of the chlorine, the process may be repeated (see p. 161).

Finally, the fabric should be rinsed thoroughly with water, to which a little ammonia may be added, washed with soap and water, again rinsed and dried.

"Anti-chlors."

In order to remove the last traces of chlorine from fabrics which have been treated with bleaching powder or hypochlorite solutions, chemical reagents which will react with the chlorine, and thus prevent its further action on the fibres, are sometimes used. Such substances are termed "*anti-chlors*," those most frequently employed being solutions of:—

Sodium bisulphite ($NaHSO_3$).
Sodium thiosulphate ($Na_2S_2O_3$).

These react with chlorine in the following manner :—

(i) $2NaHSO_3 + Cl_2 + H_2O \rightarrow Na_2SO_3 + 2HCl + H_2SO_4$.

The acids formed react with the sodium sulphite liberating sulphur dioxide.

(ii) $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$.

The chlorine, it should be noted, is converted into hydrochloric acid, and free sulphuric acid may also be formed with consequent risk to the fabric on drying.

If the bleaching process is carried out in the manner described above, the introduction of any mineral acid is avoided; the subsequent rinsing and washing in alkaline solutions may be relied on to remove the last traces of chlorine, and an "anti-chlor" is not required.

PEROXIDES: HYDROGEN PEROXIDE, SODIUM PEROXIDE.

Hydrogen peroxide probably plays an important part in the bleaching which occurs on exposure to light and air. Commercially, this substance is generally obtained in the form of an aqueous solution, prepared by the action of sulphuric acid on barium peroxide.

$$BaO_2 + H_2SO_4 \rightarrow H_2O_2 + BaSO_4.$$

Hydrogen peroxide acts as an oxidising agent by parting with one atom of oxygen, and becoming converted into water.

$$H_2O_2 \rightarrow H_2O + O.$$

It may, therefore, be represented as water *plus* one atom of available oxygen, thus

$$H_2O \,.\, O.$$

In dilute solution, hydrogen peroxide is moderately stable, but it is readily decomposed in the presence of traces of alkali, and commercial preparations usually contain a little free sulphuric acid, to prevent the solution from becoming alkaline when stored in glass bottles. This should be borne in mind in using the reagent for bleaching purposes (see p. 146).

More concentrated solutions of hydrogen peroxide (e.g. perhydrol, see below) are generally stored in bottles which are coated on the inside with paraffin wax. The solution is thus kept out of contact with the glass, and the absorption of alkali from the surface of the bottle is prevented. The

strength of an aqueous solution of hydrogen peroxide is usually given in terms of the volume of oxygen (measured at N.T.P.), liberated from one volume of the solution.

Thus in the case of a solution described as "10 *volume*," one volume of the solution should, on decomposing, give ten volumes of oxygen, measured at N.T.P. (see also p. 144).

The strength of such a solution, in terms of grams of hydrogen peroxide per 100 c.c., can readily be calculated in the following manner:—

100 c.c. of 10 vol. solution will give 1000 c.c. oxygen at N.T.P.

1 litre of hydrogen at N.T.P. = 0·0896 gm.
1 „ oxygen „ = 0·0896 × 16 gms.
= 1·43 gms.

Hence 100 c.c. of 10 vol. solution yield 1·43 gms. oxygen.

The equation

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
$$2 \times 34 \qquad 2 \times 16$$
$$34 \qquad 16$$
$$17 \qquad 8$$

shows that

8 parts of oxygen are obtained from 17 parts H_2O_2.

∴ 1·43 gms. „ „ „ $\frac{17}{8} \times 1{\cdot}43$

$= \underline{3{\cdot}03}$ gms. H_2O_2.

Hence 100 c.c. of "10 volume" hydrogen peroxide solution contain 3·03 gms. of H_2O_2.

Hydrogen peroxide is generally sold either as a 10, or as a 20 volume solution.

More concentrated solutions, e.g. "100 volume" (about 30 per cent.), sold as "perhydrol," can also be obtained.

Commercial preparations of hydrogen peroxide, however, become more unstable as the concentration increases. As even a 10 volume solution is too concentrated for bleaching purposes, there is nothing to be gained by procuring solutions of greater concentration.

Pure hydrogen peroxide is relatively stable in concentrated solutions, but tends to decompose in the presence of small quantities of impurities, such as are usually found in commercial preparations.

Determination of the Amount of Hydrogen Peroxide or of "Available Oxygen" in a Solution of Hydrogen Peroxide.

The amount of hydrogen peroxide, or of "available oxygen," in a solution of hydrogen peroxide, can be determined by several different methods:—

I. *By Determining the Amount of Iodine Liberated from an Acidified Solution of Potassium Iodide.*—Hydrogen peroxide, like other oxidising agents, liberates iodine from an acidified solution of potassium iodide, and if considerable excess of sulphuric acid is present, the reaction may be made use of quantitatively.

$$\underset{\substack{34\\17}}{H_2O_2} + 2HI \rightarrow \underset{2 \times 127}{2H_2O} + \underset{127}{I_2}$$

The iodine thus liberated can be titrated with decinormal sodium thiosulphate solution, as described under "bleaching powder" (see p. 137).

The above equation shows that

17 parts H_2O_2 liberate 127 parts iodine,

and since

1 c.c. N/10 sodium thiosulphate = 0·0127 gm. iodine,

$\therefore$ 1 c.c. N/10 sodium thiosulphate = 0·0017 gm. H_2O_2.

Or, since 17 parts H_2O_2 give 8 parts "available oxygen,"

1 c.c. of N/10 thiosulphate = 0·0008 gm. "available oxygen".

If the strength of an approximately 10 volume solution of hydrogen peroxide is required, dilute the solution 1 in 5, and to 10 c.c. of the diluted solution * add 10 c.c. of a 10 per cent. solution of potassium iodide and 30 c.c. of dilute sulphuric acid. After standing for a few minutes, titrate the liberated iodine with decinormal thiosulphate (see p. 137).

II. *By Measuring the Volume of Oxygen Liberated on Treating with an Acidified Solution of Potassium Permanganate.*—Hydrogen peroxide and potassium permanganate are both

* 10 c.c. of 10 vol. H_2O_2 = 0·3 gm.
Therefore 10 ,, ,, diluted 1 in 5 = 0·06 gm.
1 c.c. N/10 thiosulphate = 0·0017 gm. H_2O_2.

$$\text{Therefore } 0{\cdot}06 \text{ gm. } H_2O_2 = \frac{0{\cdot}06}{0{\cdot}0017} \text{ c.c. N/10 thiosulphate}$$

$$= 31{\cdot}2 \text{ c.c.}$$

Thus 10 c.c. of the diluted solution is a convenient quantity to work with.

oxidising agents, but when mixed together in an acid solution, the "available oxygen" present in the permanganate combines with the "available oxygen" of the hydrogen peroxide, with the formation of free oxygen, and the consequent reduction of both reacting substances.

$$(K_2O \cdot 2MnO \cdot 5O) + 5H_2O \cdot O + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

This reaction can be employed for the quantitative determination of the available oxygen in a solution of hydrogen peroxide.

A known volume of the solution is decomposed with excess of permanganate in the presence of sulphuric acid, and the volume of oxygen liberated is measured.

It will be seen from the above equation that half the volume of oxygen liberated comes from the hydrogen peroxide and the other half from the permanganate.

Hence *half* the measured volume of oxygen gives the volume of oxygen obtained from the hydrogen peroxide, and one volume of a 10 *volume* solution of hydrogen peroxide should, on decomposing with permanganate, give 20 *volumes* of oxygen (measured at N.T.P.).

The determination of available oxygen by this method can be conveniently carried out in a *Lunge nitrometer*. (For description and method of using the apparatus see p. 42.)

Fill the nitrometer with water and adjust (P) (see Fig. 4) so that the water nearly fills (A) when the level of the liquid in the two tubes is the same.

Measure into the flask (D) a known volume of the hydrogen peroxide solution (see below) and add about 20 c.c. of dilute sulphuric acid.

Fill the small tube (T) with a saturated solution of potassium permanganate and suspend in (D). Attach the flask (D) to the capillary (C) and proceed as described on page 44.

Since the nitrometer is graduated to measure only 50 c.c. of gas, the quantity of hydrogen peroxide used must be so regulated that the volume of gas liberated does not exceed this amount.

About 20-30 c.c. gas is the most convenient volume to work with.

If the "available oxygen" in an approximately 10 volume solution is to be determined, 10 c.c. of this solution should

give 100 c.c. available oxygen (N.T.P.), or 10 c.c. of this solution on decomposing with potassium permanganate should give 200 c.c. available oxygen (N.T.P) (see p. 144).

Hence if the 10 volume solution is diluted 1 in 10, and 10 c.c. of the diluted solution decomposed with permanganate, the volume of gas evolved should be about 20 c.c., and this is therefore a suitable quantity to work with in the nitrometer.

The quantity of potassium permanganate added must be in excess of that required to decompose the hydrogen peroxide.

If the solution becomes decolorised during the experiment the quantity of permanganate added was insufficient and the experiment must be repeated, using more permanganate or decreasing the amount of peroxide.

III. *By Determining the Amount of Potassium Permanganate Required to Decompose a Known Volume of the Solution.*— Instead of measuring the volume of oxygen liberated on decomposing with potassium permanganate, the strength of *dilute* solutions of hydrogen peroxide may be determined by direct titration with a decinormal solution of potassium permanganate in presence of sulphuric acid.

$$\begin{array}{ccccc} H_2O_2 & + & O & \rightarrow & H_2O + O_2 \\ 34 & & 16 & & \\ 17 & & 8 & & \end{array}$$

(See also equation, p. 144.)

The above equation shows 8 parts of available oxygen from the permanganate will decompose 17 parts of hydrogen peroxide.

A decinormal solution of potassium permanganate contains 0·8 gm. of available oxygen per litre.

Therefore 1 c.c. N/10 $KMnO_4$ = 0·0008 gm. available oxygen.

Or 1 c.c. N/10 $KMnO_4$ = 0·0017 gm. H_2O_2.

A measured volume of the hydrogen peroxide solution is acidified with dilute sulphuric acid, and decinormal potassium permanganate is run in from a burette, until a faint permanent pink colour due to a slight excess of permanganate is obtained.

(The strength of the hydrogen peroxide should be the same as that employed in Method I., see p. 143.)

Use of Hydrogen Peroxide as a Bleaching Agent.

As a bleaching agent hydrogen peroxide is slow in action, and is chiefly used with wool and silk, since these fabrics should not be bleached with chlorine (see p. 138).

For this purpose a 10 volume solution of the peroxide may be diluted 1 in 10 (i.e. a solution obtained containing 0·3 per cent. of hydrogen peroxide, see p. 142).

If hydrogen peroxide alone is used, the solution should be rendered just alkaline with ammonia, since the peroxide decomposes more readily in the presence of alkali, and at the same time any free acid in the solution is neutralised.

The articles to be bleached may be left in the diluted solution for half an hour to an hour, and should then be dried rather slowly, preferably by free exposure to light and air.

If the bleaching is not satisfactory the process may be repeated.

If the peroxide is used in conjunction with potassium permanganate an *acid* solution is required (see p. 153).

In this case any free mineral acid in the solution should first be neutralised by the addition of a slight excess of ammonia, and the solution then acidified with dilute acetic acid.

Sodium Peroxide.

Sodium peroxide (Na_2O_2) is prepared by heating sodium in a current of air or oxygen, and is sometimes used as a substitute for hydrogen peroxide, or as a source of this substance.

If sodium peroxide is mixed with a small quantity of water there is a brisk evolution of oxygen, and sodium hydroxide is formed.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2.$$

If added to a considerable bulk of water, the peroxide dissolves without noticeable evolution of oxygen, and the solution behaves as an alkaline solution of hydrogen peroxide,

$$\underset{\substack{78\\39}}{Na_2O_2} + 2H_2O = 2NaOH + \underset{\substack{34\\17}}{H_2O_2}$$

The oxidising action of sodium peroxide is therefore essentially the same as that of hydrogen peroxide, and the sodium compound may be regarded as a convenient means of storing hydrogen peroxide in a compact form.

It is important to remember, however, that caustic soda is produced when sodium peroxide is treated with water, and before such a solution is used for bleaching fabrics it should first be made just acid with dilute acid, and then rendered faintly alkaline with ammonia (see p. 146).

Determination of Available Oxygen in Sodium Peroxide.—The amount of available oxygen in sodium peroxide may be determined by any of the methods described under hydrogen peroxide.

The equation given on page 146 shows that

39 parts of Na_2O_2 will yield 17 parts H_2O_2.

Or, expressed in terms of "available oxygen,"

39 parts Na_2O_2 contain 8 parts of "available oxygen".

Hence 1 c.c. of N/10 sodium thiosulphate is equivalent to 0·0039 gm. Na_2O_2.

Or 1 c.c. of N/10 potassium permanganate is equivalent to 0·0039 gm. Na_2O_2. (See pp. 143 and 145.)

Thus in making a determination, either by iodine and thiosulphate (p. 143) or by titration with potassium permanganate (p. 145), a solution containing 3-4 gms. per litre of the sample can be conveniently employed.

In using the nitrometer for the determination of this substance, the following considerations should be borne in mind :—

39 parts of pure Na_2O_2 should yield 8 parts (by weight) of oxygen.

32 gms. oxygen occupy 22·4 litres at N.T.P.

$\therefore$ 39 gms. Na_2O_2 should yield $\frac{22{\cdot}4}{4}$ litres oxygen (N.T.P.).

Or, on decomposing with potassium permanganate,

39 gms. Na_2O_2 should yield $\frac{22{\cdot}4}{4} \times 2$ litres oxygen. (See p. 144.)

Or 0·039 gm. Na_2O_2 should yield 11·2 c.c. oxygen.

Or 0·039 × 3 = 0·117 gm. Na_2O_2 should yield 11·2 × 3 = 33·6 c.c. oxygen.

Hence the weight of Na_2O_2 used should not exceed 0·10-0·12 gm.

The Use of Sodium Peroxide as a Bleaching Agent.—If a solution of sodium peroxide is used as a source of hydrogen peroxide for bleaching, a solution containing 0·7 gm. of Na_2O_2 per litre will furnish approximately the same amount

of available oxygen as the dilute solution of hydrogen peroxide mentioned above. (See equation, p. 146.) The solution should be treated as described on p. 146.

PERSALTS—SODIUM PERBORATE.

The use of sodium perborate, $NaBO_3 . 4H_2O$, as a bleaching agent for laundry work appears to be fairly general, and preparations sold as "bleachers" or "stain removers" often contain this substance (see p. 75).

Sodium perborate can be prepared by treating a saturated solution of borax, containing an equivalent quantity of sodium hydroxide, with excess of hydrogen peroxide. The salt separates out as large transparent crystals of $NaBO_3 . 4H_2O$.

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 \rightarrow 4NaBO_3 + 5H_2O$$

Sodium perborate.

Perborates can also be obtained by the electrolysis of a concentrated solution of borates, and this method has been patented as a manufacturing process.

In aqueous solution sodium perborate behaves like a mixture of hydrogen peroxide and borate.

At ordinary room temperature the solution is fairly stable, but oxygen is liberated by boiling, or by acidifying the solution.

$$2NaBO_3 \rightarrow 2NaBO_2 + O_2$$
$$2NaBO_3 + H_2SO_4 + 2H_2O \rightarrow Na_2SO_4 + 2H_3BO_3 + O_2.$$

The bleaching action of the perborate therefore depends, as in the case of hydrogen peroxide, on the liberation of "available oxygen".

$$\underbrace{2NaBO_3 . 4H_2O}_{2 \times 154 \quad 77} \rightarrow 2NaBO_2 + O_2 + 8H_2O \qquad 32 \quad 8$$

The equation shows that 77 parts of crystalline perborate yield 8 parts of available oxygen, and are therefore equivalent to 17 parts of hydrogen peroxide (see p. 142).

Quantitative Analysis of Sodium Perborate.

The formula of sodium perborate may be conveniently expressed as

$2NaBO_3 . 4H_2O$	or Na_2O	B_2O_3	O_2	$8H_2O$
2×154	62	70	32	
154	31	35	16	

The Na_2O and B_2O_3 may be determined as described under borax (see p. 39), and the available oxygen by one of the methods described under hydrogen peroxide (see pp. 143-145).

The formula shows that as regards its content of Na_2O and B_2O_3, *a decinormal* solution of the perborate should contain 15·4 *gms. per litre.*

Since, however, the substance is not very readily soluble in water to this extent, a solution containing 10 gms. per litre may be used, or if the titrations are carried out with twentieth normal solutions, a solution of half this concentration may be employed.

As regards its oxidising action, since 15·4 parts $NaBO_3 . 4H_2O$ yield 1·6 parts available oxygen, or 7·7 parts $NaBO_3 . 4H_2O$ yield 0·8 parts available oxygen, a decinormal solution of the perborate should contain 7·7 gms. per litre of crystalline perborate.

It is important to remember, however, in making a determination of available oxygen that the solution must be prepared in the *cold*, since oxygen is evolved on heating, and as the process of solution is slow under these conditions it is advisable to work with a more dilute solution of the perborate, i.e. about 5 gms. per litre (see also p. 150).

If the nitrometer is used, considerations similar to those given on page 147 show that the quantity of perborate used should not exceed 0·2 gm.

Examination of Preparations Containing Sodium Perborate (Perborin Products).

Sodium perborate possesses the advantage that it can be incorporated with soap and washing powders, and several preparations of this kind containing soap, sodium carbonate, sodium silicate and sodium perborate are now on the market.

These preparations are sold wholesale under the name of "perborin products," "Perborin" itself being sodium perborate, and "Perborin M" a mixture of soap, alkali and sodium perborate, which can be used as a combined washing and bleaching agent.

The general method of examining such preparations has already been described under soap powders, but in the case of perborin products special attention should be paid to the detection and determination of the perborate.

The presence of perborate may be detected in the following manner :—

I. *Examine for the Presence of Borate* (see p. 35).—The presence of fatty acids will not interfere with the tumeric test for borate, but precipitation tests with silver nitrate, etc., cannot be carried out in the presence of soap (see p. 64).

II. *Examine for the Liberation of Available Oxygen.*—To portions of the solution acidified with dilute sulphuric acid add :—

(*a*) A few drops of potassium iodide solution ; the liberation of iodine, as shown by the production of a blue colour on the addition of starch paste, indicates the presence of available oxygen.

$$\underset{\text{Perborate.}}{NaBO_2 . O} + 2HI \rightarrow \underset{\text{Metaborate.}}{NaBO_2} + H_2O + I_2$$

(*b*) A few drops of a dilute solution of potassium permanganate. In the presence of available oxygen the permanganate will be decolorised and oxygen liberated.

$$5NaBO_2 . O + K_2O . 2MnO . 5O + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5NaBO_2 + 5O_2.$$

The sodium metaborate thus produced will be converted into orthoboric acid by the excess of sulphuric acid.

$$2NaBO_2 + H_2SO_4 + 2H_2O \rightarrow Na_2SO_4 + 2H_3BO_3.$$

Determination of Sodium Perborate in Perborin Products.—In the absence of other oxidising agents, a determination of available oxygen may be taken as a measure of the amount of perborate present in the preparation, on the basis that 0·8 gm. of available oxygen corresponds to 7·7 gms. of perborate.

This is the most convenient method of determining the amount of perborate in preparations containing perborate and other alkaline substances, e.g. sodium carbonate, soap, etc.

The available oxygen may be determined by direct titration with decinormal permanganate ; the nitrometer should *not* be used if the mixture contains sodium carbonate owing to the liberation of carbon dioxide on acidifying.

Since the amount of perborate in such preparations is often relatively small and may vary considerably in quantity, difficulty is sometimes experienced in preparing a solution of suitable strength for titration ; to obviate this the following method may be employed :—

Fill a weighing bottle about two thirds full of the finely

powdered substance * and weigh. Add 50 c.c. of dilute sulphuric acid to 200-300 c.c. of distilled water in a large beaker. Carefully shake a little of the powder into the acidified water, stir well with a glass rod, and run in decinormal permanganate from a burette until a faint permanent pink colour is obtained. If only a small volume of permanganate is required to reach this end point, shake in a little more of the powder, stir well, and repeat the process until the volume of permanganate added is not less than 9-10 c.c.

Reweigh the bottle and its contents, and so obtain the weight of the substance used in the determination.

The method of working is shown in the following example :—

Example.

A washing powder containing perborate gave the following results on analysis :—

Weight of weighing bottle and powder = 19·763 gms.
" " " " after experiment = 17·629 gms.
Weight of powder used = 2·134 "
Volume of decinormal permanganate used = 9·8 c.c.
1 c.c. of N/10 $KMnO_4$ = 0·0008 gm. available oxygen
= 0·0077 " $NaBO_3 . 4H_2O$ (see p. 149).

Hence

2·134 gms. of powder contain 9·8 × 0·0077 gms. perborate.

Or 100 gms. of powder contain $\frac{9{\cdot}8 \times 0{\cdot}0077}{2{\cdot}134} \times 100$

$= \underline{3{\cdot}57}$

The powder contains 3·57 per cent. of perborate.

Use of Sodium Perborate for Bleaching Purposes.

In using sodium perborate as a bleaching agent in laundry work, acetic acid is usually added to facilitate the liberation of the oxygen (see p. 148); this also renders the substance more readily soluble.

Since 77 parts $NaBO_3 . 4H_2O$ are equivalent in oxidising

* These preparations are usually sold in the form of a powder, but are sometimes mixed with water to form a paste.

In the latter case some of the substance should be transferred to a small beaker provided with a short glass rod, and the beaker, rod and contents weighed.

Portions of the mixture can then be detached by means of the rod and mixed with the acidified water. When a suitable volume of permanganate has been added the beaker, rod and contents are reweighed.

power to 17 parts H_2O_2 (see p. 148), a solution of sodium perborate, equivalent in oxidising or bleaching power to the dilute hydrogen peroxide solution (0·3 per cent.) described on page 146, will be obtained by mixing $77 \times \frac{3}{17} = 13{\cdot}5$ gms. of perborate with 1000 c.c. of water, and adding dilute acetic acid until the solution is just acid.

This solution may be used in the same manner as the hydrogen peroxide solution.

POTASSIUM PERMANGANATE (IN CONJUNCTION WITH OTHER REAGENTS).

Potassium permanganate is not usually regarded as a bleaching agent; it may, however, as described originally by Hartley, be effectively employed *in conjunction with other reagents* for the removal of stains.

In *acid* solution potassium permanganate decomposes in the presence of oxidisable material, the reaction being represented thus:—

$$\underbrace{K_2O \cdot 2MnO \cdot 5O}_{K_2Mn_2O_8} + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O.$$

Such a solution is frequently used as an oxidising agent, but is *unsuitable for bleaching purposes*, owing to the presence of free sulphuric acid.

In neutral solution potassium permanganate reacts with oxidisable matter, the reaction being represented thus:—

$$\underbrace{K_2O \cdot 2MnO_2 \cdot 3O}_{K_2Mn_2O_8} + H_2O \rightarrow 2KOH + 2MnO_2 + 3O.$$

Such a solution may conveniently be used for bleaching purposes, if the manganese dioxide, which is formed during the reaction and deposited on the fabric in a hydrated form, is afterwards removed by some suitable reagent.

The reagents which may be used for this purpose are dilute solutions of the following:—

Sulphurous acid; Hydrogen peroxide, acidified with acetic acid; Oxalic acid containing a little acetic acid.

The reactions of these substances with managanese dioxide can be represented by the following equations:—

Sulphurous Acid.

$$\underbrace{MnO \cdot O}_{MnO_2} + H_2SO_3 \rightarrow MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O$$

MnO_2 Brown. — Manganese sulphate (colourless in dilute solution).

Hydrogen Peroxide and Acetic Acid.

$$MnO.O + H_2O.O + 2CH_3COOH \rightarrow MnO + 2CH_3COOH + O_2 + H_2O \rightarrow (CH_3COO)_2Mn + O_2 + 2H_2O$$

Manganese acetate (colourless in dilute solution).

Oxalic Acid and Acetic Acid.

$$MnO.\boxed{O} + \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2CH_3COOH$$

$$\rightarrow MnO + 2CH_3COOH + H_2O + 2CO_2$$
$$\rightarrow (CH_3COO)_2Mn + 2H_2O + 2CO_2.$$

Manganese acetate.

Of these substances, sulphurous acid is the most rapid in action, and it may be satisfactorily employed for cotton and linen fabrics. It should, however, be borne in mind that any excess of sulphurous acid left in the fabric is liable to become oxidised by the air to sulphuric acid, and it is necessary to wash the material thoroughly after such treatment (see p. 107).

For the same reason, it is not advisable to use sulphurous acid in the case of wool or silk, but a dilute solution of hydrogen peroxide acidified with acetic acid should be substituted.

A dilute solution of oxalic acid containing a little acetic acid may also be used, but is slow in action, and difficulty may be experienced in removing the last traces of manganese dioxide with this reagent.

Method of Bleaching with Potassium Permanganate followed by (a) Sulphurous Acid, (b) Hydrogen Peroxide and Acetic Acid.

(*a*) *Sulphurous Acid* (Cotton and Linen).—Bleaching by this method may be carried out in the following manner:—

Steep the fabric in a solution containing 1 part of solid potassium permanganate in 160 of water (or 1 oz. per gallon) for a few minutes, until a definite brown colour has been produced. Wash thoroughly with water, and whilst still wet, place the brown fabric in a solution of sulphurous acid containing 2-3 per cent. of sulphur dioxide (see p. 156). Leave the fabric in the solution until the brown colour has disappeared. Wash thoroughly in water, and if the colour has not been completely removed, repeat the process (see p. 161). Finally, wash with soap and water, and rinse in the usual manner.

(*b*) *Hydrogen Peroxide* (Silk and Wool).—Wool and silk take up permanganate more readily than linen and cotton,

and the permanganate solution used in (*a*) may with advantage be diluted with an equal volume of water, for use with wool or silk.

Proceed as described in (*a*), but substitute for the sulphurous acid solution a dilute solution of hydrogen peroxide acidified with acetic acid, and prepared as described on p. 146.

If the above directions are carefully carried out, this method will be found a very useful one in laundry practice. It is not quite so easy to apply as a chlorine process, but the risk of damaging the fabrics is much less.

It may be noted that the action of the permanganate is a selective one, and an organic stain, particularly on linen or cotton, becomes brown some time before the rest of the fabric is much coloured. On removing the fabric from the solution, it will be observed that the region of the stain is much darker in colour than the surrounding fabric.

If no such selective action is observed, there has, in all probability, been no reaction between the colouring matter and the permanganate, and the stain is therefore one that cannot be satisfactorily dealt with by this method.

Bleaching by Reduction.

As a rule, bleaching by reduction is less permanent than that brought about by oxidation, since the colour is liable to return to some extent on exposure to light and air, and often returns when the bleached material is treated with soap or alkali. The action of light is to favour the absorption of oxygen from the air, and to restore the reduced compound to its original condition.

The most important reducing agents used for bleaching, are the following :—

Sulphur dioxide, or sulphurous acid, sodium metabisulphite, sodium hydrosulphite (sodium hyposulphite), titanous chloride ("stripping salts"), stannous chloride.

SULPHUR DIOXIDE AND SULPHUROUS ACID.

Bleaching may be effected either by gaseous sulphur dioxide or by an aqueous solution of the gas. In either case the bleaching action is due to the oxidation of sulphur dioxide to sulphuric acid, in the presence of water, the hydrogen, which is liberated in the nascent condition, reacting with the colouring matter to form a colourless substance.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2.$$

If gaseous sulphur dioxide is to be used as the bleaching agent, the moistened fabric is exposed to the fumes of burning sulphur.

$$S + O_2 \rightarrow SO_2.$$

The reagent is more usually employed in the form of an aqueous solution; such a solution may be prepared by acidifying a sulphite with sulphuric acid, or by passing sulphur dioxide* into water until a saturated solution is obtained.

This latter method is more satisfactory from the point of view of bleaching, since, with a freshly prepared solution, the presence of any free acid, other than sulphurous acid, is avoided. The amount of sulphur dioxide present in such a solution can readily be determined by direct experiment.

Determination of Sulphur Dioxide.

If excess of iodine is added to a *dilute* solution of sulphur dioxide, the following reaction takes place:—

$$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4.$$

This reaction can be utilised for the quantitative determination of sulphur dioxide. It is, however, important to remember that the above reaction is of the nature of a *reversible reaction*, and does not take place quantitatively, unless the solutions are sufficiently dilute.

In *concentrated* solution, sulphuric acid and hydriodic acid mutually decompose one another, the reaction going in the reverse direction, thus:—

$$2HI + H_2SO_4 \rightarrow I_2 + H_2SO_3 + H_2O.$$

If the strength of a saturated solution of sulphur dioxide is required, the solution should be diluted 1 part in 10, and the determination may then be made in the following manner:—

Carefully deliver 10 c.c. of the dilute sulphurous acid solution into 25 c.c. of decinormal iodine, keeping the end of the pipette just below the surface of the iodine solution, thus avoiding any loss of sulphur dioxide on mixing.

Should the iodine become decolorised during this operation, the experiment should be repeated, using 50 c.c. of decinormal iodine, or a portion of the sulphurous acid solution may be diluted to a known volume with water, and 10 c.c. of diluted solution used for the determination.

* For this purpose a siphon of liquid sulphur dioxide is convenient.

Determine the amount of iodine present in the solution by titration with decinormal thiosulphate (see p. 137).

The difference between the amount of iodine added, and that left in the solution, gives a measure of the sulphur dioxide present.

From the equation—

$$H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + 2HI$$

$H_2O . SO_2$

64 2×127

32 127

it is seen that 32 parts of SO_2 react with 127 iodine, and since 1 c.c. of N/10 thiosulphate = 0·0127 gm. iodine, therefore 1 c.c. ,, ,, = 0·0032 ,, SO_2.

Hence for each c.c. of decinormal iodine used up, 0·0032 gm. SO_2 was present.

Example.—A solution of sulphurous acid was diluted 1 in 10.

Ten c.c. of the diluted solution were added to 25 c.c. of iodine solution (N/10 approx.) and the excess of iodine was found to be equivalent to 10·3 c.c. of N/10 sodium thiosulphate solution (Factor = 1·02).

Twenty-five c.c. of the iodine solution were found by experiment to be equivalent to 24·8 c.c. of N/10 thiosulphate (Factor = 1·02).

The sulphur dioxide present in 10 c.c. of diluted solution is thus equivalent to $(24·8 - 10·3) \times 1·02$ c.c. N/10 thiosulphate

$= 14·5 \times 1·02$ c.c. ,, ,,

$= 14·5 \times 1·02 \times 0·0032$ gms. SO_2.

Therefore 100 c.c. of the diluted solution

$= 14·5 \times 1·02 \times 0·032$ gm. SO_2

$= 0·473$ gm. of SO_2.

Or, 100 c.c. of the original solution contain 4·73 gms of SO_2.

The Use of Sulphurous Acid as a Bleaching Agent.

For bleaching purposes a solution containing from 2-3 per cent. of sulphur dioxide may be used.

As already indicated (see p. 155) such a solution is best prepared by passing sulphur dioxide gas into water; it is obvious, however, that in this case it is difficult to determine, except by experiment, the amount of sulphur dioxide present, and it should also be noted that the solution is unstable and will lose sulphur dioxide on keeping.

If water is saturated with the gas at room temperature and used immediately, it may be diluted with an equal volume of water for bleaching purposes; this as a rule gives a solution of about the required strength.

If convenient means of generating sulphur dioxide gas are not available, a solution of sulphurous acid for bleaching may be prepared by dissolving 100 gms. of sodium sulphite ($Na_2SO_3 . 7H_2O$) in a litre of water to which 20 c.c. of concentrated sulphuric acid have been added;* but in this case special care must be taken to rinse the fabric thoroughly before drying (see p. 107).

Sulphurous acid is most effective when used in conjunction with potassium permanganate (see p. 153).

SODIUM METABISULPHITE AND SODIUM HYPOSULPHITE.

These substances are occasionally used in laundry work for the removal of stains, but their use is chiefly confined to the "stripping" or bleaching of articles which are to be subsequently dyed.

Sodium Metabisulphite or Sodium Disulphite, $Na_2S_2O_5$, is obtained by supersaturating a solution of caustic soda with sulphur dioxide,

$$2NaOH + 2SO_2 \rightarrow \underbrace{Na_2S_2O_5}_{Na_2SO_3 . SO_2} + H_2O.$$

It decomposes gradually in the air, taking up oxygen and giving off sulphur dioxide,

$$2Na_2S_2O_5 + O_2 \rightarrow 2Na_2SO_4 + 2SO_2.$$

Its bleaching action is similar to that of sulphur dioxide.

Sodium Hyposulphite or Hydrosulphite ($Na_2S_2O_4$).

This compound should be carefully distinguished from *sodium thiosulphate*, $Na_2S_2O_3$, which is sometimes *incorrectly* described as sodium hyposulphite. The thiosulphate gives off

$$* \; Na_2SO_3 . 7H_2O + H_2SO_4 \rightarrow Na_2SO_4 + 8H_2O + SO_2$$

252	98	64
126	49	32
100	$\frac{49}{126} \times 100 = 38{\cdot}8$	$\frac{32}{126} \times 100 = 26{\cdot}0$

Thus 100 gms. of $Na_2SO_3 . 7H_2O$ require 38·8 gms. H_2SO_4 and yield 26 gms. of SO_2.

Since sp. gr. $H_2SO_4 = 1{\cdot}8$, 38·8 gms. $= \frac{38{\cdot}8}{1{\cdot}8} = 21{\cdot}5$ c.c. Excess of acid should be avoided, so 20 c.c. may be added.

sulphur dioxide on treating with an acid, but is not by itself a bleaching agent,

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S.$$

Zinc dissolves in sulphurous acid without the evolution of hydrogen, and it may be shown that the following reaction takes place :—

$$2H_2SO_3 + Zn = \underset{\text{Zinc hyposulphite.}}{ZnS_2O_4} + 2H_2O.$$

If a strong solution of sodium acid sulphite is shaken with zinc, and sulphur dioxide passed into the mixture, the corresponding sodium salt is obtained, thus :—

$$2NaHSO_3 + SO_2 + Zn \rightarrow \underset{\text{Sodium hyposulphite.}}{Na_2S_2O_4} + ZnSO_3 + H_2O.$$

The zinc may be removed by the addition of excess of lime, and the sodium salt crystallised from the solution as $Na_2S_2O_4 . 2H_2O$.

The hyposulphites are strong reducing agents ; both in the solid state, when moist, and in aqueous solution they rapidly absorb oxygen, and become converted into metabisulphites, which are further decomposed as shown on page 157.

$$\underset{\text{Hyposulphite.}}{2Na_2S_2O_4} + O_2 \rightarrow \underset{\text{Metabisulphite.}}{2Na_2S_2O_5}.$$

The hydrated salt $Na_2S_2O_4 . 2H_2O$ is unstable, but on boiling with alcohol the water of crystallisation is removed, and the anhydrous salt ($Na_2S_2O_4$), which is moderately stable, is obtained. This salt is sold under the name " Hydrosulphite," and the preparation usually contains about 90 per cent. of the hyposulphite.

Other preparations sold under such names as " Rangalite " and " Hydraldite " contain hyposulphite combined with formaldehyde. They are stable under ordinary conditions, but are decomposed by steam and the hyposulphite liberated.

For bleaching purposes a 1 per cent. solution of the hyposulphite may be employed, and is sometimes used in laundry practice for bleaching fabrics which have been over-blued with methylene blue (see p. 167), this colour being difficult to remove by other methods.

STANNOUS CHLORIDE AND TITANOUS CHLORIDE.

These substances, like the sulphur compounds just dealt with, are chiefly employed for the removal of colouring matter

from fabrics previous to dyeing, and are only occasionally used in laundry practice.

Titanous chloride ($TiCl_3$) is sold in the form of a concentrated solution under the name of "*stripping salts*," though some preparations thus described contain chiefly stannous chloride ($SnCl_2$) which is less powerful in its action.

In the case of titanous chloride a yellow stain may be formed on the fabric, and in order to prevent this, hydrochloric acid is usually added to the stripping solution, or to the first rinsing water.

"Stripping salts" and stannous chloride require careful handling if damage to the fabric is to be avoided, and should only be used when less drastic methods have been tried and failed.

NOTES ON THE REMOVAL OF STAINS FROM TEXTILE FABRICS.

It is extremely difficult to give any precise directions for the treatment of the various stains likely to be met with in the ordinary course of laundry work, since the method to be employed depends, not only on the nature of the stain, but also on the nature and colour of the fabric on which the stain occurs.

Each stain really requires to be dealt with individually, but some of the more important factors which should be taken into consideration in dealing with stains on textile fabrics may be briefly discussed here. This will also serve to indicate the general lines on which a suitable choice of method may be made, and the precautions which it is necessary to take in order to avoid injury to the fabric or to its colour.

Nature of the Stain.—Any colouring matter deposited on a fabric, other than that intentionally added as dye, may be regarded as a stain. Hence the stains met with on fabrics are extremely varied in character. Some of the more frequently occurring stains and the reagents which may be employed for their removal are dealt with later (see p. 162).

Nature of the Fabric.—As already indicated (see Textile Fibres) vegetable fibres (cotton, linen) are not so injuriously affected by the use of bleaching agents as animal fibres (wool, silk); linen, it should be remembered, is more readily attacked by oxidising agents than cotton (see p. 124).

Solutions containing mineral acids should not be used for wool and silk, and if used for cotton and linen special care

should be taken to ensure the complete removal or neutralisation of the acid before drying the fabric (see p. 107).

If an acid bath is necessary, acetic acid should be used where possible. Chlorine bleach should not be used for wool or silk. Other oxidising agents, e.g. hydrogen peroxide, sodium perborate, etc., may be used for these fabrics, or potassium permanganate, followed by hydrogen peroxide (see p. 153), may also be employed.

*Colour of the Fabric.**—In the case of coloured articles, if a sample of the material is available for the purpose, a trial experiment should be made with the bleaching agent to be employed, in order to see if the colour of fabric is injured by such treatment.

It is important to bear in mind that animal fibres (wool and silk) dye more readily than vegetable fibres, and that dyes are as a rule faster on wool and silk than on linen and cotton. Hence reagents which will remove stains from coloured wool and silk without injury to the colour, may completely destroy the colour of cotton goods, e.g. dilute potassium permanganate followed by hydrogen peroxide has usually little or no effect on coloured wool and silk fabrics, whereas coloured cotton goods are often completely bleached by the action of these reagents.

General Method of Procedure.

Preliminary Treatment.—In the case of "washing fabrics," the stain should be dealt with before washing with soap and water in the usual manner, as this process may in some cases tend to fix the colour on the fabric. Cotton goods which are heavily dressed with starch, etc., should be treated with lukewarm water to remove as much of the dressing as possible before applying the bleaching agent. (The starch may also be removed by treating with dilute malt extract, see Vol. II.)

In cases where they are at all likely to be effective, simple remedies should be tried first, before resorting to the use of a bleaching agent; e.g. tea stains, fruit juice stains, etc., especially if fresh, can often be removed by sponging with lukewarm water or water containing a little borax.

* *Colour of the Fabric.*—These remarks are based chiefly on observations made on coloured fabrics obtained before the war. At the present time many of the dyes are more fugitive than formerly, and coloured fabrics need to be handled with great caution. This state of affairs is, however, probably only temporary.

If the article is such that it cannot subsequently be washed as a whole with soap and water, it is advisable to use *soft* water, as it is less likely to leave a mark on drying.

The Use of Bleaching Agents.—Methods of preparing solutions of the various bleaching agents of suitable concentration for laundry work, and the precautions to be taken in using such solutions have already been dealt with individually (see pp. 138-158).

The following general observations will serve to emphasise some of the more important points.

Prolonged steeping in the bleaching solutions is to be avoided, except in the case of dilute solutions of hydrogen peroxide (see p. 146).

After steeping for a few minutes in the bleaching solutions the fabric should be thoroughly rinsed with water. The treatment with the bleaching agent may then be repeated, two or three times, if necessary, rinsing with water between each treatment, until the stain is removed.

In this manner stains can be more rapidly and effectively removed than by prolonged treatment with the bleaching solution, and the risk of damage to the fabric is considerably less.

Finally, the article should be washed with soap and water, again rinsed, and dried.

Bleaching agents will sometimes remove most of colouring matter of a stain, leaving a slight colour or mark which does not yield to further treatment with the bleaching solution. These marks will, in many cases, be found to disappear completely during the subsequent washing with soap and water.

Hence if a stain is found to be only partially removed after several treatments with a bleaching agent, it is advisable to try washing with soap and water before resorting to an alternative method of bleaching.

Though it is impossible to predict exactly the effect which a bleaching agent will have on any particular colour or fabric, solutions of bleaching agents, if prepared and used with all necessary precautions, in the manner described in the foregoing pages, may as a general rule be employed under the following conditions :—

Bleaching agents which may be used for :—

White.	*Coloured.**
Cotton and Linen.	
All.	Hydrogen peroxide or sodium perborate. Acids, e.g. oxalic, citric, etc., for iron stains.
Silk and Wool.	
Hydrogen peroxide, perborate, etc. Potassium permanganate followed by hydrogen peroxide and acetic acid.	Hydrogen peroxide, perborate, etc. *Usually* potassium permanganate followed by hydrogen peroxide and acetic acid — colour should, if possible, be tested.

COMMON STAINS.

Vegetable and Fruit Juice Stains are often removable by water, or water containing a little borax or ammonia. If these fail, a dilute solution of an oxidising agent may be tried. The oxidising agent should be selected with reference to the nature and colour of the fabric (see above).

Tea, Coffee, Cocoa, etc.—Proceed as above. In some cases, especially if milk is present, a greasy mark may be left; this can usually be removed by washing with soap and water, or one of the methods described under Dry-cleaning may be employed (see p. 175).

Iron Stains usually occur in the form of ferric oxide or "iron mould," and may be produced by the presence of iron in the water, or in parts of the machinery with which the fabrics come in contact, and also by the decomposition of unsuitable laundry blues, i.e. blues containing Prussian blue (see p. 166).

Inks also usually contain iron salts (see p. 163), and iron mould may be produced by the partial decomposition of these compounds during the process of washing. Iron mould is usually removed by treatment with an acid, the iron being thereby converted into a soluble salt. Solutions of oxalic

* See note, p. 160.

acid, potassium acid oxalate (salts of sorrel or salts of lemon *), citric acid (or lemon juice), are most generally used for this purpose.

Since the iron is already in a fully oxidised condition, it is useless to try oxidising agents, but reducing agents, by converting the iron to the ferrous condition, will often facilitate its removal by an acid.

A solution of oxalic acid (up to 10 per cent.), containing a little sulphurous acid, generally gives satisfactory results. The action is rather slow, but may be hastened by warming.

Ink Stains.—*Writing Inks* vary considerably in character, but mostly contain iron salts of gallo-tannic acid, with or without added colouring matter and gum.

The various methods advocated for the removal of ink stains depend either on: (1) dissolving out the iron compound with a suitable acid (as described under Iron Stains); or (2) on the use of a bleaching agent. For this purpose, potassium permanganate, followed either by sulphurous acid or hydrogen peroxide, may be conveniently employed.

Method (2) is more rapid in its action, and generally more satisfactory than method (1); it cannot, however, be employed for coloured cotton materials (see p. 160).

Red Inks were at one time prepared from a decoction of Brazil wood, or sometimes from cochineal (see "Colouring Matters in Foods," Vol. II.), but these colouring matters have now been almost entirely displaced by preparations of aniline dyes, e.g. eosin and Congo-red, and the stains produced by such inks are often extremely difficult to remove.

Eosin marks, if quite fresh, can sometimes be removed by treating with ammonia, or a saturated solution of borax. Failing this, a reducing agent, e.g. sulphurous acid or sodium hydrosulphite, may be tried, since in some forms the colouring matter can be reduced by this means to a colourless leuco-compound.

Congo-red can be distinguished from other reds by treatment with dilute acids which changes the colour from red to blue.

Treatment with reducing agents (hydrosulphite) will sometimes remove the stain, but the colour is often only partially removed.

* Potassium acid oxalate, KHC_2O_4, and potassium quadroxalate, $KHC_2O_4 . H_2C_2O_4 . 2H_2O$, are sold as salts of lemon or salts of sorrel.

Marking Inks.—Marking inks may be divided into two classes: (*a*) those which require the application of heat to bring up the colour; (*b*) those which do not require heating.

Inks belonging to class (*a*) are usually solutions of an easily reducible silver compound, e.g. ammoniacal silver nitrate or tartrate, with a little added colouring matter. On heating, the silver compound is reduced, and fixed upon the fabric as a dark insoluble deposit.

Stains produced by such inks may be removed by painting the stain with a solution of iodine (in potassium iodide), the silver is thereby converted into silver iodide, and the iodide and excess of iodine can then be removed by treatment with a solution of sodium thiosulphate. The reactions involved are as follows:—

$$2AgI + 3Na_2S_2O_3 \rightarrow \underset{\text{(Soluble double salt).}}{Ag_2S_2O_3 . 2Na_2S_2O_3} + 2NaI$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6.$$

Several treatments may be necessary for the complete removal of the stain, and sometimes a faint yellowish mark is left; this mark can usually be removed by painting with a dilute solution of potassium cyanide.

If preferred, potassium cyanide* may be used instead of iodine; the silver is converted to silver cyanide, which is afterwards removed by thiosulphate.

$$2AgCN + 3Na_2S_2O_3 \rightarrow Ag_2S_2O_3 . 2Na_2S_2O_3 + 2NaCN.$$

Inks belonging to class (*b*) are usually preparations of aniline dyes, e.g. aniline black, obtained by the oxidation of aniline. Stains produced by these inks cannot be removed by the above method, but are sometimes removable by treatment with potassium permanganate followed by sulphurous acid or hydrogen peroxide.

Scorch Marks are produced by the surface of the material becoming overheated during the process of drying or ironing. Such marks are frequently dealt with as stains. It should be remembered, however, that scorching implies the burning or charring of some of the surface fibres of the material, and that the removal of scorch marks entails the removal of the partially destroyed surface fibres, and not simply the removal of colouring matter.

* Owing to the poisonous nature of this substance, great care must be exercised in its use.

If somewhat extensive charring of the fibres has taken place, it is impossible to remove the burnt or damaged fibres without causing further injury to the fabric ; but if the charring has only been slight, and is entirely confined to the surface fibres, the mark will sometimes yield to suitable treatment, e.g. washing with soap and water and gently rubbing. This is more particularly the case with white linen or cotton goods, which may be safely boiled with soap and water for some time without risk of injury to the fabric.

Oxidising agents, e.g. hydrogen peroxide, perborate, etc., are sometimes added to the soap and water, though it appears doubtful whether their addition facilitates the removal of the damaged fibres to any marked extent.

Grease Marks, Paint, etc.—These marks are usually removed by one or other of the solvents used for " dry-cleaning," and are therefore dealt with in that section (see p. 175).

Blue Marks.—White goods which have been washed several times in soap and water tend to become slightly yellowish in colour ; to counteract this effect, and restore the original white appearance, such articles are usually rinsed in water containing some form of blue colouring matter.

If too much colouring matter is added the articles become stained with blue, or over-blued, and it then becomes necessary to remove the excess of colouring matter.

The method to be employed depends on the nature of the " blue " used, and a brief description of colouring matters most commonly used in laundry " blues " may be given here.

LAUNDRY BLUES.

The principal colouring matters used for this purpose are the following :—

Ultamarine, indigo or indigotin, Prussian or Berlin blue, liquid or soluble blues.

Ultramarine or *Lapis lazuli* is an inorganic colouring matter composed of a double silicate of aluminium and sodium combined with sulphur.

The exact constitution of the compound has not yet been determined, but it can be prepared artificially by heating together clay, sodium sulphate, charcoal and sulphur. It is possible to obtain white and green ultramarine as well as the blue variety, and a compound very similar to ultramarine, but containing cobalt, is sometimes sold as *Chinese Blue.*

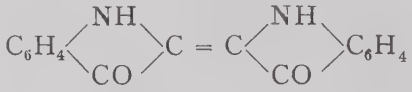
Ultramarine is not soluble in water, but if finely ground suspends well in water, and articles steeped in this suspension become evenly coated with blue.

Ultramarine is readily decomposed by dilute acids, gelatinous silica and finely divided sulphur being deposited and sulphuretted hydrogen evolved.

Hence, if the material has become stained with ultramarine, the excess of colouring matter can be removed by treating with a dilute solution of acid, preferably acetic acid.

Indigo or Indigotin, a dye formerly obtained from the juices of certain plants (*Indigoferæ*), now prepared artificially from naphthalene.

Its constitution may be represented thus :—



Indigo.

Indigo is insoluble, but can be suspended in water in the same way as ultramarine, and for laundry purposes it is generally used in this form.

On reduction indigo takes up two atoms of hydrogen, forming a colourless leuco-body, *indigo-white*. In alkaline solutions this substance is rapidly reconverted into indigo by atmospheric oxidation.

This reaction is made use of in dyeing with indigo, since owing to its insolubility in water it cannot be used directly in the dye bath.

The dye is first reduced by hydrosulphite (see p. 157), and the fabric then soaked in an alkaline solution of the reduced dye ; on exposure to the air indigo is formed and fixed on the fibres. For this reason indigo is sometimes described as a "*developed dye*" or a "*vat-dye*".

Indigo-carmine.—Indigo dissolves in fuming sulphuric acid forming indigo-sulphonic, or sulphindigotic acid, which is soluble in water, the sodium salt of this acid being sold as *indigo-carmine*. This substance may be used instead of indigo, but the colours obtained are more fugitive.

Indigo stains can be removed by treatment with a reducing agent, e.g. sulphurous acid or sodium hydrosulphite, the indigo being thereby reduced to indigo-white.

Prussian or Berlin Blue (*Ferric ferrocyanide*) is sometimes used in laundry blues, but is most unsuitable for this purpose

since it is decomposed by alkalis with the formation of ferric hydroxide.

$$Fe_4'''(Fe(CN)_6)_3 + 12NaOH \rightarrow 4Fe(OH)_3 + 3Na_4Fe(CN)_6.$$

Prussian blue.

Thus fabrics treated with Prussian blue are liable to develop iron stains, particularly if, owing to insufficient rinsing, they contain soap or soda when "blued".

Iron stains produced by the decomposition of Prussian blue should be treated in the manner already described (see p. 162).

Prussian blue is insoluble in water, but like ultramarine and indigo it will suspend in water if finely ground.

Liquid or Soluble Blues.—Blue colouring matters which are soluble in water and used in the form of an aqueous solution are sold as "liquid" or soluble blues. These preparations have the advantage over the insoluble colouring matters dealt with above, in that they give a more even colouring to the fabric.

Liquid blues may contain indigo-carmine (see p. 166), but more frequently are solutions of aniline dyes, e.g. methylene blue, and in the event of over-blueing with such solutions considerable difficulty may be experienced in removing the excess of colour. Reducing agents should be tried (see p. 158).

Some of these blues also have the further disadvantage that an acid bath is necessary to set the colour on the fabric, with the consequent possibility of damage to the fibres on drying.

Chapter VI.

DRY-CLEANING.

Dry-cleaning is a term used to describe the process of cleaning fabrics with certain organic liquids which act as solvents of grease.

A considerable amount of the dirt, which adheres to the fabric by means of the grease, will be removed during the process, but the cleansing action depends essentially on dissolving out the grease. The solvent does not penetrate into the fibres, i.e. the fabric does not become "wetted," as in the ordinary process of washing, and dry-cleaning is seldom satisfactory in the case of really dirty articles.

The colours of fabrics are, as a rule, quite unaffected by the solvents used for dry-cleaning, and the method is therefore especially suitable for fabrics which are likely to be damaged or partially bleached by the ordinary process of washing with soap and water.

Most of the solvents which are used for dry-cleaning are immiscible with water, and fabrics which are to be dry-cleaned should first be well dried and then freed as far as possible from loose dirt and dust.

LIQUIDS USED FOR DRY-CLEANING.

Theoretically, any liquid which has a solvent action on grease might be used for the purpose of dry-cleaning.

In working on a large scale, however, the choice of solvent is dependent on various practical considerations. If an extremely volatile solvent is used, i.e. a solvent with a very low boiling-point (e.g. ether, b.p. = 36° C.), it is impossible to avoid a considerable loss of solvent by evaporation during the cleaning process, and the method is therefore wasteful. If, on the other hand, a high boiling-point solvent is used, prolonged heating or "stoving" is necessary to remove the last traces of solvent from the goods.

The boiling-point of the solvent should lie preferably be-

tween 80° and 120° C., with as small a range of boiling-point as possible, since if the solvent tends to fractionate there will be undue loss of the lighter fractions by evaporation, whilst prolonged "stoving" will be necessary to remove the last traces of the higher fractions.

For practical purposes the principal solvents used for dry-cleaning may be divided into two groups, those which are inflammable at ordinary temperatures and those which are not.

Inflammable Solvents.

In using these solvents all operations must be carried out well away from any flame or open light, and the bottles containing such solvents should be clearly labelled to indicate that the contents are inflammable.

Ether, Diethylether, $C_2H_5 . O . C_2H_5$, b.p. 36° C., is frequently used as a solvent for fats, but is too volatile and inflammable to be satisfactory as a dry-cleaning solvent.

Benzine, Light Petroleum, Petrol,* is the solvent most extensively used on a large scale. It is obtained by the fractional distillation of petroleum and is composed of hydrocarbons of the paraffin series of which heptane, C_7H_{16}, is the chief constituent.

Benzine should be carefully distinguished from benzene or benzol (C_6H_6, see p. 170).

Benzine is usually sold according to its specific gravity, which should be 0·72-0·78, and this gives some indication of its nature, but it is necessary to point out the specific gravity only gives the *average* density of the paraffins present, and gives no indication as to whether the specific gravities and boiling-points of these paraffins vary only over a small range, or whether paraffins of low specific gravity and low boiling-point are present, mixed with those of high specific gravity and high boiling-point.

It is therefore advisable, in the case of such a solvent, to determine the range of boiling-point of the solvent, as well as its specific gravity; this may be done in the following manner:—

To Find the Range of Boiling-point of Benzine (or Petrol).—Introduce about 50 c.c. of the solvent into a small dry distilling flask fitted with a cork and thermometer, and add a few pieces of porous tile to prevent bumping.

Connect the flask to a water condenser, which by means of

* See "Chemistry of Petroleum," by Tinkler and Challenger (Crosby Lockwood & Son) for list of trade names for petroleum products.

an adapter and tightly-fitting corks, communicates with a filter flask (see Fig. 10).

The side tube of the filter flask should be provided with a rubber tube, by means of which any uncondensed vapour may be led away to a level below that of the bench.

Support the flask over an iron tray, so that in case of an accident the spreading of the inflammable liquid will be prevented.

Cautiously heat the flask with a small flame * and note the temperature at which the liquid begins to distil over. Continue heating until nearly all the liquid has distilled over, and note the highest temperature reached.

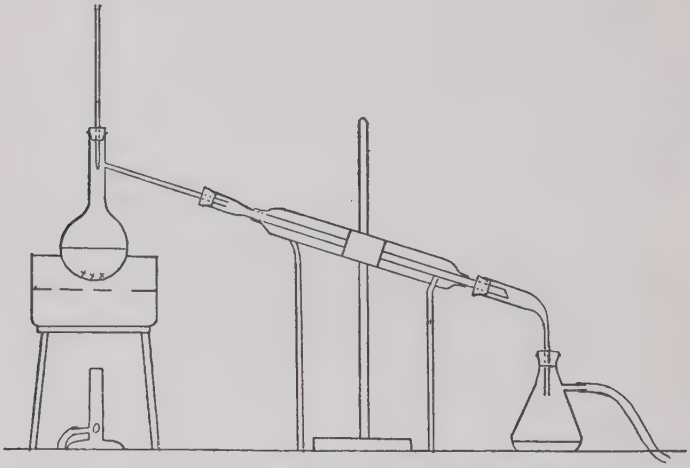


FIG. 10.—Apparatus for Distillation of Ether, etc.

If the liquid does not begin to distil over below 80° C. and the highest temperature recorded is below 120° C., the solvent may be considered as suitable for dry-cleaning purposes.

Commercial Benzene, or Benzol, (C_6H_6 and homologues), is one of the products of the distillation of coal tar, and consists essentially of hydrocarbon C_6H_6, together with small quantities of its homologues (i.e. toluene, $C_6H_5CH_3$, and o., m. and p. xylenes, $C_6H_4(CH_3)_2$).

The boiling-point of pure benzene is 80° C. and its specific gravity at 15° C. = 0·884. A good sample of commercial benzol should distil almost completely between 80° and 120° C.

* In dealing with a solvent of unknown composition it is advisable to start the heating on a water bath, see p. 172.

In the case of the so-called 90 per cent. benzol, 90 per cent. of the liquid distils below 100° C.

Benzene is a very effective solvent for grease, also for tar and paint, but its price has, until recently, prevented its more extensive use on a large scale.

Non-Inflammable Solvents.

The chlorine derivatives of some of the hydrocarbons also act as solvents for grease, and have the advantage that they are not readily inflammable at ordinary temperatures. In most cases, however, they possess anæsthetic properties and therefore need to be handled with care, whilst some of them are liable in the presence of steam to attack and corrode the metal work of the machinery with which they come in contact.

Chloroform or Trichloromethane, $CHCl_3$, b.p. 61° C., sp. gr. at 15° C. = 1·498.

This substance can be used as a dry-cleaning solvent, but is unsuitable on account of its marked anæsthetic action.

Carbon Tetrachloride or Tetrachloromethane, CCl_4, b.p. 76° C., sp. gr. at 20° C. = 1·593, may be used as a dry cleaning solvent, but its anæsthetic action and the fact that it is liable in the presence of steam to corrode iron, render it open to objection.

For reference to use of this substance in a fire extinguisher, see p. 264.

Ethylene Trichloride or Trichloroethylene, $CHCl : CCl_2$, b.p. 87° C., sp. gr. 1·49 at 4° C.

This substance is sold under the name of "*Westrosol*," and appears to be specially suitable for dry-cleaning purposes. It has slight anæsthetic properties, but is without action on metals, and has the additional advantage that its cleansing action is not injuriously affected by the presence of moisture in the fabric. The fact that it is composed of one constituent of constant boiling-point, renders the loss by evaporation considerably less than in the case of a solvent such as petrol, where a considerable loss of the low boiling-point constituents is unavoidable.

Tetrachloroethane, $C_2H_2Cl_4$, b.p. 135° C., sp. gr. at 19° C. = 1·576.

This substance is sold under the name of "*Westron*". It dissolves fats and oils readily, but like carbon tetrachloride is liable to corrode iron in the presence of steam. This fact,

combined with its relatively high boiling-point, renders it unsuitable as a solvent for ordinary dry-cleaning purposes. It may, however, be used for the removal of local grease marks, etc. (see p. 175).

EXAMINATION OF LIQUIDS SOLD FOR DRY-CLEANING.

As a rule the solvent will be labelled as inflammable or non-inflammable, as the case may be. It is advisable, however, in the case of liquids described as non-inflammable to check the accuracy of this statement by actual experiment.

Pour a few drops of the liquid into a porcelain dish, place the dish on a metal tray, and try to ignite the liquid with a lighted taper.

If the liquid does not ignite, heat it gently on a water bath for a few minutes, and again try to ignite it. If the liquid fails to ignite under these conditions it may be classified as non-inflammable at ordinary temperatures.*

Examination of Inflammable Liquids.

These will usually contain one or other of the inflammable solvents mentioned above. The more common solvents, e.g. petrol and benzene, are readily distinguished by their smell, and in most cases a determination of the boiling-point and specific gravity of the liquid will supply the necessary information as to its nature.†

The specific gravity may be determined by means of a hydrometer or the Westphal Balance,‡ and the boiling-point may be found in the manner described on page 169. In dealing with an unknown solvent, it is advisable to start the heating on a water-bath, in case any low boiling-point constituents are present, and then to continue heating over a flame *after* having *carefully dried* the outside of the flask.

It is again necessary to emphasise the fact that in carrying out experiments with these solvents, all possible precautions must be taken to avoid any possibility of liquid becoming ignited.

* See "Flash Point," p. 247.

† For other distinguishing tests between petrol and benzene see "Chemistry of Petroleum".

‡ For a description of this balance see "Chemistry of Petroleum," by Tinkler and Challenger (Crosby Lockwood & Son).

Examination of Non-inflammable Liquids.

These solvents should first be examined for the presence of chlorine, by one or other of the tests usually applied for the detection of chlorine in organic compounds, such, for example, as the following:—

Heat a piece of copper wire* in the edge of a Bunsen flame, until the green colour which is first imparted to the flame disappears. Allow the wire to cool, then dip it into the liquid and again heat it in the flame.

In the presence of chlorine a blue coloration is produced, owing to the production and volatilisation of copper chloride.

The specific gravity and boiling-point of the liquid should then be determined, when it will usually be possible to identify the liquid as one or other of the solvents mentioned above.

If the liquid distils over a considerable range of temperature, i.e. the boiling-point is not constant, it may consist of a mixture of two or more solvents, and in this case it should be fractionally distilled.

DRY-CLEANING SOAPS.

Since the solvents used for dry-cleaning act only on grease, soap is sometimes added to them with a view to increasing their cleansing power. It should be remembered, however, that soap dissolved in one of these solvents is by no means such an efficient detergent as soap dissolved in water (see p. 80).

The soap used for this purpose must be dry, or it will not dissolve readily in the solvent, and should not contain any free alkali either as caustic alkali or as alkaline salts (see p. 63).

Preparations of soap dissolved in one or other of the solvents mentioned above are sold as "dry-cleaning soaps" or "dry cleaners".

A preparation known as "*tetrapol*" is composed of soap dissolved in carbon tetrachloride, whilst "*westropol*" contains soap dissolved in "westrosol" (see p. 171).

To Show the Presence of Soap in such preparations, the solvent should be removed by evaporation, or distillation, the residue dissolved in water, and acid added to liberate the fatty acids.

* A few strands of teased asbestos dipped in powdered copper oxide, and bound together by means of a wire, may also be employed for this purpose instead of copper wire.

A quantitative experiment may be made by weighing the fatty acids obtained from a known weight of the substance.

Examination of the Solvent.—The solvent may be separated from the soap by distillation in steam (see p. 68).

The distillate should be separated as completely as possible from the water, dried over calcium chloride and redistilled.

The boiling-point should be noted and the specific gravity of the distillate determined. From these data it is usually possible to identify the solvent.

**THE REMOVAL OF GREASE MARKS.

In cases where dry-cleaning as a whole is not required, grease marks may be removed by the local application of one or other of the solvents dealt with above.

In order to prevent the spreading of the grease, the solvent should not be applied directly to the mark, but the fabric round the mark should first be saturated with the solvent.

An explanation of this method of procedure is afforded by a consideration of the phenomenon of surface tension as exhibited by liquid films.

The superficial tension in a film of oil or grease is greater than that exhibited by petrol or benzene.

Hence if the fabric round a grease mark is saturated with one of these liquids, the tension will be greatest in the region of the grease. The mixture of grease and solvent will be drawn towards the grease, and the grease will be forced towards the centre of the mark, where it can be absorbed by a layer of blotting paper or other absorbent material placed in contact with the fabric.

If, on the other hand, the liquid is applied to the middle of the grease mark, the grease, followed by a mixture of grease and solvent, will spread out into the surrounding fabric, leaving the clean solvent in the centre.

To demonstrate the effect of applying the solvent directly to the grease mark the following experiment may be made :—

Experiment to Demonstrate the Effect of Applying the Solvent Directly to a Grease Mark.—Carefully clean a white, flat-bottomed dish, e.g. a developing dish, and just cover the bottom with clean distilled water to which a few drops of methyl-orange or other colouring matter have been added. Dip a glass rod into alcohol and lightly touch the surface of the water in the dish with the rod.

The surface tension of water being greater than that of a mixture of alcohol and water, the water moves away from the drop of alcohol on all sides, dragging some of the alcohol with it, with the result that a bare patch is formed and shows up white in the region where the alcohol was introduced.

In a similar manner if a solvent is applied directly to a grease mark, a clean patch will be left in the centre of the mark where the solvent was applied, but the grease will spread out into the clean portions of the fabric, leaving a greasy rim or mark round the edge of the region treated with the liquid.

These considerations will also apply to other solvents which may be used instead of benzene or petrol, and the following method may be employed for the removal of a grease mark with any of the usual dry-cleaning solvents :—

To Remove a Grease Mark by Means of a Solvent, e.g. Petrol, Benzene, etc.

Spread the fabric right side downwards on a pad of clean blotting-paper or rag.

Apply the solvent with a piece of clean absorbent material or sponge, *first* to the fabric surrounding the mark until this is well saturated with the solvent, and *then* to the mark itself, working gradually from the edges of the mark towards the centre, and continue to rub gently until nearly all the solvent has evaporated.

Repeat the treatment, if necessary, until the mark is completely removed.

To Remove a Grease Mark by the Application of Heat.

Instead of using a solvent, grease marks can sometimes be removed by the application of heat, and here also the surface action of the grease film plays an important part.

The surface tension of a film of grease decreases with rise in temperature, and if a hot iron is applied to a grease mark on a piece of fabric, the grease will tend to move away from the heated surface towards the cooler portions of the fabric. Hence to remove a grease mark by the application of heat proceed in the following manner :—

Place the fabric right side downwards on a pad of blotting-paper or absorbent rag. Gently warm the surface of the material in the neighbourhood of the mark with a hot iron.

The grease will be driven away from the heated surface and will collect in the absorbent material underneath.

Removal of Marks made by Machine Oil, etc.

If grease mixed with a considerable amount of other dirt, e.g. machine oil, etc., is deposited on a fabric, the marks cannot be satisfactorily dealt with by the methods described above, since the grease only will be affected by the application of heat or of solvents.

The method most frequently advocated for the removal of such marks is first to rub more fat or oil into the mark, to loosen the cake of dirt, and then to remove both the grease and dirt by washing in a good lather of soap and water.

This process may, however, be modified with advantage by rubbing in oleic acid instead of fat or oil, the oleic acid being subsequently converted to ammonium oleate by neutralisation with ammonia.

In this manner ammonium oleate is formed in the fabric, a copious lather is produced, and the mark can readily be washed out.

To remove a mark made by machine oil, etc., proceed in the following manner :—

Apply a little oleic acid to the mark, and rub it well into the fabric. Dip the material into a dilute solution of ammonia (bench reagent), rub gently until a good lather is obtained and continue to wash until the mark has completely disappeared. Rinse well in clean water and dry.

Paint and Tar Marks.

Either benzol or turpentine may be used for paint marks. For *tar*, benzol is the most suitable solvent. In order to prevent the spreading of the mark the solvent should in all cases be applied in a manner similar to that described for the removal of grease marks. In all cases the mark should be removed as soon as possible.

Chapter VII.

AIR ANALYSIS, ETC.

DETERMINATION OF AQUEOUS VAPOUR AND CARBON DIOXIDE IN AIR.

In connection with all problems of ventilation, the determination of the amount of aqueous vapour and carbon dioxide in the air is of great importance. Various methods are adopted for the determination of these constituents of the air, the simplest in principle being a method by which both constituents are determined at the same time, by drawing a measured volume of air, by means of an aspirator, through U tubes containing pumice soaked in concentrated sulphuric acid, to absorb water vapour, and soda lime to absorb carbon dioxide. This method requires considerable time, and other methods which can be carried out more rapidly are described in detail later.

The increase in the weight of the U tube containing pumice and sulphuric acid gives the weight of water vapour, and the increase in weight of the soda lime tube gives the weight of carbon dioxide in the volume of air which has passed through the apparatus. In the actual determination, precautions would have to be taken to prevent the absorption of water vapour from the aspirator by the soda lime or sulphuric acid.

The temperature and pressure at the time of the experiment are noted.

From the results of such determinations the relative humidity of the air and the percentage by volume of carbon dioxide in the air are calculated as follows:—

Relative Humidity or Hygrometric State of the Air.—The relative humidity

$$= \frac{\text{amount of water vapour in a given volume of air}}{\text{amount of water vapour in this volume of air if saturated with aqueous vapour.}}$$

The weight of water vapour in a given volume of air may

be determined, and the weight of water vapour in this volume of air, if saturated with aqueous vapour, may be calculated.

Thus by noting the temperature at the time of the experiment, the pressure of saturated aqueous vapour at this temperature can be found on reference to tables.

For example, if 30 litres of air were drawn through the U tubes, in 30 litres of air saturated with water vapour at 15° C. (since the tension of saturated aqueous vapour at 15° C. = 13 mm.) there are 30 litres of aqueous vapour at 15° C. and 13 mm. pressure.

$$\text{At } 0^\circ \text{ C. and } 760 \text{ mm. this} = 30 \times \frac{273}{288} \times \frac{13}{760} \text{ litres.}$$

From the relation 22·4 litres of aqueous vapour at 0° C. and 760 mm. = 18 gms., the weight of this volume of water vapour is found, and from this weight and the weight of aqueous vapour found by experiment, the relative humidity may be calculated.

Carbon Dioxide.—From the relation 44 gms. of carbon dioxide = 22·4 litres at 0° C. and 760 mm., the volume of carbon dioxide at 0° C. and 760 mm. corresponding to the weight of carbon dioxide determined may be calculated. This volume, corrected to the temperature and pressure of the air at the time of the experiment, gives the volume of carbon dioxide in the volume of air which passes through the apparatus.

The result is usually expressed as per cent. by volume of carbon dioxide, or as parts per 10,000.

The amount of carbon dioxide in air varies from about 3·5 parts per 10,000 (0·035 per cent.) in country air to 40 or more parts per 10,000 (0·4 per cent.) in the air of a crowded room.

DEW POINT.

Water vapour is invariably a constituent of the air, but the amount present in a given volume of air varies very considerably from time to time. Only very rarely is the air completely saturated with water vapour. In this case the water vapour and liquid water are in equilibrium, and no more water vapour will be taken up by the air.

Under ordinary conditions, however, water is present in the air as an unsaturated vapour, and more and more water can be taken up by a given volume of the air, until it becomes saturated with aqueous vapour. When the air is not saturated

with water vapour the pressure exerted by the latter depends on the amount of water vapour present. The pressure exerted by a saturated vapour, however, depends only on the temperature, and in the case of water varies from 4·6 mm. at 0° C. to 760 mm. at 100° C. The higher the temperature, the greater is the amount of aqueous vapour which can be taken up by a given volume of air.

[For a description of the method employed for measuring the pressures of saturated and unsaturated vapours, etc., see "Chemistry of Petroleum," by Tinkler and Challenger" (Crosby Lockwood & Son), pp. 88-92.]

By cooling air containing unsaturated water vapour, a temperature, known as the *dew point*, will be reached at which there is sufficient water vapour present in the air for the latter to become saturated with it. Any diminution of the temperature below this point leads to the separation of liquid water from the air in the form of dew.

The deposition of dew on solid objects at night is explained by the fact that these objects become cooler than the air owing to loss of heat by radiation. The temperature of the air in their immediate neighbourhood is so far reduced, that the water vapour present is sufficient to saturate the air, and the excess of moisture is deposited as dew.

The dew point may be determined experimentally by means of a condensing hygrometer, the principle of which is as follows :—

The air is cooled locally, and the temperature noted at which separation of moisture takes place. The temperature of the air is then allowed to rise and the point at which the dew disappears is noted. The mean of these two temperatures is taken as the dew point.

Determination of the Dew Point by Means of the Regnault Hygrometer.

The apparatus consists of a large test tube, the lower portion of which is covered with thin silver foil. The tube is fitted with a cork carrying a thermometer, a glass tube, which reaches nearly to the bottom of the apparatus, and a short glass tube which is attached to a water pump or aspirator some distance away from the apparatus.

Ether is poured into the test tube to a point well above the silver foil.

On turning on the tap of the pump or aspirator, a stream of air is drawn slowly through the ether, which increases its rate of evaporation, and thus causes a diminution of temperature.

The temperature at which dew appears on the silver foil is noted. The water pump is then disconnected and the temperature at which the dew disappears is observed. The mean of these two temperatures is taken as the dew point. The experiment is repeated several times and the average reading taken as the dew point.

In order to obtain accurate results, the apparatus should be at some distance from the observer and the observations made by means of a telescope.

Relative Humidity from the Dew Point.

Since the relative humidity of the air

$$= \frac{\text{amount of water vapour actually present in the air}}{\text{amount of water vapour present in the air if saturated}},$$

and since the amount of water vapour present in the air is proportional to the pressure which it is exerting, the relative humidity may be expressed as

$$= \frac{\text{Pressure of water vapour in the air}}{\text{Pressure of water vapour in the air if saturated}}.$$

The pressure of water vapour in the air is the pressure of *saturated* water vapour at the *dew point* of that air. This pressure and that of saturated water vapour at the temperature of the air may be found on reference to tables.

Example.—The temperature of the air at the time of an experiment was 15·5° C. and the dew point 10·5° C.

Pressure of saturated aqueous vapour at 15·5° = 13·1 mm.

Pressure of saturated aqueous vapour at 10·5° = 9·5 mm.

Relative humidity $= \frac{9{\cdot}5}{13{\cdot}1} = 0{\cdot}725$, or the air is 72·5 per cent. saturated with water vapour.

For temperatures from 60° to 70° F. a relative humidity of about 0·73, or 73 per cent. saturation, is the most suitable standard from the point of view of health.

Wet and Dry-Bulb Thermometers.

Two similar thermometers are mounted on a stand side by side. The bulb of one of them is kept continuously moistened

with water by means of a cotton fabric, which dips into a small reservoir containing water. The drier the air, the more rapidly the water on the cotton evaporates, and owing to this evaporation, and consequent absorption of heat, the temperature registered by the wet-bulb thermometer is always less than that registered by the dry-bulb thermometer. If, however, the air is saturated with aqueous vapour the temperatures indicated by both thermometers are the same, as evaporation is then impossible.

The temperature indicated by the wet-bulb thermometer is *not* the dew point, but the latter may be calculated from the readings of both thermometers by use of a so-called Glaisher factor. These factors have been obtained experimentally, by comparing the results obtained for the dew point by means of a condensing hygrometer with the readings obtained with wet- and dry-bulb thermometers.

For table of Glaisher factors see "Hygiene," by Notter and Firth (Churchill).

The formula adopted for the calculation of the dew point from the readings of the wet- and dry-bulb thermometers is as follows:—

Dew point = dry-bulb reading F.° – (difference between dry- and wet-bulb readings F.°) × Glaisher factor.

Example:—

Reading of dry-bulb thermometer = 70° F.
„ wet-bulb „ = 50° F.
Glaisher factor for dry-bulb reading of 70° F. = 1·8.
Dew point = 70 – (70 – 50) × 1·8
= 70 – 36
= 34° F.

The relative humidity may be calculated by converting the temperatures 70° F. and 34° F. into the corresponding centigrade temperatures, and finding the pressures of saturated aqueous vapour, in millimetres of mercury, at these temperatures from a table of pressures of saturated aqueous vapour.

By making use of a table of pressures of saturated water vapour in inches of mercury, corresponding to temperatures Fahrenheit, the same result for the relative humidity will of course be obtained.

Another table for calculating the dew point from the readings of the wet- and dry-bulb thermometers in degrees centigrade, shows the relation between the dry-bulb reading, the

difference between the wet- and dry-bulb readings, and the pressure of saturated aqueous vapour at the dew point.

Thus if temperature registered by the dry-bulb thermometer is 10° C. and the temperature registered by the wet-bulb thermometer is 7° C. from the table the pressure of water vapour at the dew point is 5·7 mm. which corresponds to a dew point of 3° C.

The relative humidity in this case is $\frac{5·7}{9·1} = 0·626$ (9·1 mm. being the pressure of saturated aqueous vapour at 10° C.).

Note on Relative Humidity.

In connection with this subject the following considerations should be noted.

The relative humidity of the air of a room varies greatly according to the method employed for the artificial heating of the room. If the air itself is warm, as is the case in all methods of heating by means of convection currents, the relative humidity is very considerably reduced owing to this rise of temperature. Consequently, an excessive amount of water may evaporate from the surface of the skin or from the mucous membrane of the throat and nose. This objection is not met with when the room is warmed by means of radiant heat, in which case the temperature of the air itself rises very slowly.

Thus, if the temperature of the air of a room is initially 15·5° C. and the dew point 10·5° C., the relative humidity of the air is $\frac{9·5}{13·1} = 0·725$ (see p. 180).

If now the temperature of the air rises to 25° C., the moisture content of the air remaining the same, the relative humidity becomes $\frac{9·5}{23·5} = 0·404$ (23·5 mm. being the pressure of saturated aqueous vapour at 25° C.).

It is often found, for example, that a temperature of 75° F. in certain parts of the world, where the relative humidity of the air is usually low, can be withstood as easily as one of 55° F. in another part of the world where the relative humidity is high. The explanation of this is as follows :—

Under ordinary conditions heat is lost from the body by radiation, convection and conduction, and also owing to the evaporation of water at its surface.

It will be readily understood that at the temperature of 55° F., if the air is nearly saturated with water vapour, very little heat will be lost owing to the evaporation of water, although much heat will be lost by radiation, etc., due to the large difference between the temperature of the body, 98·4° F., and that of the air, 55° F. On the other hand, with the temperature at 75° F. comparatively little heat is lost by radiation, etc., but since the relative humidity of the air in this case is less, much more heat is lost owing to evaporation of water than in the former case. If, however, at this temperature the relative humidity increases, the air becomes very oppressive.

The Kata-Thermometer.

The ordinary wet- and dry-bulb thermometers which are employed in determining the relative humidity of the air (p. 170), give no indication of *the rate of loss* of heat due to evaporation. Thus in a closed room, in which the moisture content of the air is high, the oppressive feeling of the air becomes very much less marked if a fan is set in motion. When the air of such a room is still, the evaporation of water from the surface of the body takes place very slowly, on account of the slow diffusion of moisture from the air immediately surrounding the body. If, however, the air near the body is being changed, the rate of evaporation will necessarily be increased, with a consequent feeling of relief, although of course the moisture content of the air is not diminished by the air being set in motion.

An instrument known as the Kata-Thermometer has been invented by Prof. Leonard Hill, by means of which it is possible to compare the rates of cooling in air under different conditions. The construction of the instrument and the method employed for its use are as follows :—

Two thermometers, having large bulbs filled with coloured alcohol, have marks on the stems corresponding to 110°, 100° and 90° F., and another mark just above the bulb. One of the thermometers, the wet-bulb instrument, has a woven cotton covering over the bulb. This material holds the amount of water necessary for taking an observation.

The thermometers are immersed in water at about 110° F., so that the mark just above the bulb of each instrument is level with the surface of the water. When the reading of each thermometer is about 110° F. and the threads are continuous,

the instruments are withdrawn, the one rapidly dried and the excess of moisture jerked off from the other (wet-bulb thermometer). The instruments are then placed in the clips provided in the case, and the time required for the temperatures, as indicated by the thermometers, to fall from 100° F. to 90° F. taken by means of a watch. The time of cooling (from 100° F. to 90° F.) of the wet- and dry-bulb instruments at about body temperature is thus found.

It has been found that the most suitable conditions of heating and ventilation of a room are obtained when the dry-bulb thermometer takes about 2 mins. 30 secs., and the wet-bulb 50 secs. in cooling from 100° F. to 90° F.

In a later form of the apparatus a factor is supplied for each thermometer.

Dividing this factor by the number of seconds taken for the thermometer to cool from 100° F. to 95° F., gives the rate of cooling at body temperature in mille-calories per square centimetre per second.

The value obtained with the wet-bulb thermometer gives the rate of cooling by radiation, convection and evaporation, and with the dry-bulb thermometer the rate of cooling by radiation and convection. The difference between the two results gives the rate of cooling by evaporation.

By using the thermometer, with and without the cotton covering, the same instrument may be used for both readings.

THE DETERMINATION OF CARBON DIOXIDE IN THE AIR BY PETTENKOFER'S METHOD.

In this method a given volume of air (5 to 10 litres) is treated with a measured volume of a solution of barium or calcium hydroxide, by which the carbon dioxide contained in the air is absorbed with the formation of barium or calcium carbonate.

Barium and calcium carbonates are not decomposed by a dilute solution of oxalic acid; so that if a given volume of the barium or calcium hydroxide solution is titrated with a solution of oxalic acid of known concentration, before absorption of carbon dioxide, and a similar volume of the solution is titrated after absorption of the carbon dioxide, the difference in the volume of acid required gives the volume of oxalic acid solution equivalent to the amount of carbon dioxide in the given volume of air. From this the percentage of carbon

dioxide, or the amount by volume of carbon dioxide per 10,000 of air may be calculated.

Solutions required:—

1. *A Standard Solution of Oxalic Acid.*

From the equations

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$
171 gms. 44 gms. or 22,400 c.c. at N.T.P.

$$Ba(OH)_2 + (COOH)_2 . 2H_2O \rightarrow Ba(COO)_2 + 4H_2O.$$
171 gms. 126 gms.

171 gms. of barium hydroxide absorb 22,400 c.c. of CO_2 at N.T.P., and are neutralised by 126 gms. of crystallised oxalic acid, $H_2C_2O_4 . 2H_2O$.

$\therefore$ 22,400 c.c. of CO_2 at N.T.P. are equivalent to 126 gms. $H_2C_2O_4 . 2H_2O$.

$\therefore$ 1 c.c. of CO_2 at N.T.P. is equivalent to

$$\frac{126}{22,400} = 0.005625 \text{ gm. } H_2C_2O_4 . 2H_2O.$$

Thus if the solution of oxalic acid employed contains 0·005625 gm. of crystallised oxalic per c.c. (i.e. 5·625 gms. per litre), the difference in the volume of the oxalic acid solution required for a given volume of the solution of barium hydroxide, before and after the absorption of the carbon dioxide, gives at once the number of c.c. of carbon dioxide at N.T.P. contained in the given volume of air.

Weigh out $\frac{5·625}{4}$, i.e. 1·4063 gms., of crystallised oxalic acid, dissolve in recently boiled, cold, distilled water and dilute to 250 c.c.: 1 c.c. of this solution = 1 c.c. CO_2 gas at N.T.P.

This dilute solution of oxalic acid should be used as soon as possible after being made up, as it undergoes decomposition on being kept.

2. *A Solution of Barium Hydroxide.*—Filter about 200 c.c. of a saturated solution of barium hydroxide through a fluted filter paper. Dilute the filtrate with an equal volume of recently boiled, cold, distilled water. Place the solution in a bottle, stopper securely and mix thoroughly by shaking.

Determination of Carbon Dioxide.

For a first analysis it will be advisable to employ air collected in the open. Clean two large bottles, of 5 to 10 litres capacity, fitted with rubber bungs. Measure the capacity of the

bottles by means of a litre cylinder, rinse out with recently boiled, cold, distilled water and drain thoroughly.

The air to be examined is blown through the bottles for some minutes, by means of a bellows fitted with a rubber tube reaching to the bottom of the bottles, and the bottles are closed securely by means of the rubber bungs.

Place 100 c.c. of the solution of barium hydroxide, measured with a pipette,* in each of the bottles, and immediately replace the rubber bungs and the stopper of the bottle containing the barium hydroxide solution.

Place the bottles on their sides and turn them round frequently during the next 20 minutes, so as to keep the sides moistened with fresh portions of the barium hydroxide solution.

Whilst the absorption of the carbon dioxide is in progress, the titration of the barium hydroxide solution with the standard solution of oxalic acid (blank experiment) should be carried out.

Measure out 25 c.c. of the baryta solution (see footnote *re* use of pipette) and titrate with the standard solution of oxalic acid, using *phenolphthalein* as indicator. Repeat the titration twice more and take the mean of the last two readings.

Owing to the continuous absorption of carbon dioxide from the air by the barium hydroxide solution, the titrations should be carried out as rapidly as is consistent with accuracy. If preferred, for the second and third titrations most of the oxalic acid solution required may be run from the burette into a flask, before the 25 c.c. of the baryta solution are added. The titration is then finished by the addition of more oxalic acid solution from the burette.

Calculate the volume of the standard solution of oxalic acid which would be required for the neutralisation of 100 c.c. of the barium hydroxide solution.

When the air in the bottles has been in contact with the solution of barium hydroxide for at least 20 minutes, remove 25 c.c. of the solution from one of the bottles by means of a pipette, to the lower end of which a piece of glass tubing is

* Owing to the fact that expired air contains about 100 times as much carbon dioxide as ordinary fresh air, great care should be exercised to prevent access of expired air to the barium hydroxide solution during the experiment. On this account it is advisable to make use of the water pump for drawing up the solutions into the pipettes. Do not on any account blow through a pipette, but remove the last drop by placing the first finger of the right hand over the upper end of the pipette and the left hand over the bulb, when, owing to the expansion of the air, the last drop of liquid is expelled.

attached, if necessary, and titrate with the standard oxalic acid solution as before. Repeat the titration with two further portions of 25 c.c. and take the mean of the last two readings.

Calculate the volume of oxalic acid solution required for the 100 c.c. of the barium hydroxide solution.

Repeat the experiment for the solution in the other bottle.

The difference in the volume of oxalic acid solution, required for 100 c.c. of the barium hydroxide solution in the blank and test experiments, gives the number of c.c. of carbon dioxide at N.T.P. in the volume of air contained in each bottle.

The volume of air in contact with the solution of barium hydroxide is the volume of the bottle less 100 c.c. occupied by the solution.

Correct these volumes of carbon dioxide to the temperature and pressure in the laboratory at the time of the experiment, and calculate in each case the percentage of carbon dioxide in the air under examination. Express the result also as parts of carbon dioxide per 10,000.

Example :—

Blank experiment. Temperature 13° C. Pressure 752 mm.

Mean result, 25 c.c. barium hydroxide solution = 19·2 c.c. standard oxalic acid solution.

∴ 100 c.c. barium hydroxide solution = 76·8 c.c. standard oxalic acid solution.

Test :—

Mean result, 25 c.c. barium hydroxide solution after absorption of CO_2 required 18·23 c.c. standard oxalic acid solution.

∴ 100 c.c. barium hydroxide solution after absorption of CO_2 required 72·9 c.c. standard oxalic acid solution.

Difference, 76·8 − 72·9 = 3·9 c.c.

1 c.c. oxalic acid solution = 1 c.c. CO_2 at N.T.P.

Volume of bottle to rubber bung = 10,150 c.c.

∴ Volume of air employed = 10,150 − 100 = 10,050 c.c.

∴ 10,050 c.c. of air at 13° C. and 752 mm. contain 3·9 c.c. CO_2 at N.T.P.

$$3{\cdot}9 \text{ c.c. } CO_2 \text{ at N.T.P.} = 3{\cdot}9 \times \frac{285}{273} \times \frac{760}{752} = 4{\cdot}12 \text{ c.c. at } 13^\circ \text{ C. and } 752 \text{ mm.}$$

Thus 10,050 c.c. of air contain 4·12 c.c. of CO_2 ;

or, 100 c.c. of air contain $\frac{4{\cdot}12 \times 100}{10{,}050} = 0{\cdot}0409$ c.c. CO_2;
or, the air contained 4·09 parts of CO_2 per 10,000.

Various other methods are employed for the determination of carbon dioxide in air, but the Pettenkofer method is the most reliable.

In the Lunge and Zeckendorf method air is blown, by means of a rubber compression bulb, through a very dilute solution of sodium carbonate containing phenolphthalein. By the action of the carbon dioxide contained in the air, the sodium carbonate is converted into bicarbonate which is not alkaline to phenolphthalein. From the number of compressions of the bulb required for the discharge of the colour, and by reference to a table, the amount of carbon dioxide per 10,000 of air is obtained.

For calculations relating to amount of fresh air required for removal of carbon dioxide produced by respiration, etc., see page 203.

THE DETERMINATION OF OXYGEN IN THE AIR.

This determination may be carried out, either by means of the Bunté burette, or the Hempel apparatus. The oxygen is absorbed by means of a mixture of solutions of pyrogallol, $C_6H_3(OH)_3$, and potassium hydroxide, or by a solution of sodium hyposulphite, $Na_2S_2O_4$.

THE BUNTÉ BURETTE.

The construction of the apparatus is shown in Fig. 11.

By means of the two-way tap C, connection is made either between A and E, or B and E.

The capacity of the burette from the point marked O to the upper stop-cock is 100 c.c.

F is an aspirator containing water. This should be supported well above the level of the bench.

Before commencing an experiment, make sure that the taps C and D have recently been lubricated and are securely wired in. Fill the burette with water from the aspirator * by

* Instead of an aspirator a rubber tube attached to an ordinary water tap may be used for this purpose. In this case it is important always to turn off the metal water tap before the burette tap, otherwise the rubber tubing is forced off owing to the pressure of the water.

attaching the rubber tube to the lower end, and opening the taps D and C, so that the water passes into the cup B up to one of the marks 20 c.c. or 25 c.c. on B.

Close the taps C and D. Remove the tube of the aspirator from the burette, open the tap C, so that A is in connection with E, and allow water to run from the burette through D until the level falls slightly below the point marked O.

Close the tap D and close C completely. There is now slightly more than 100 c.c. of air in the burette under atmospheric pressure.

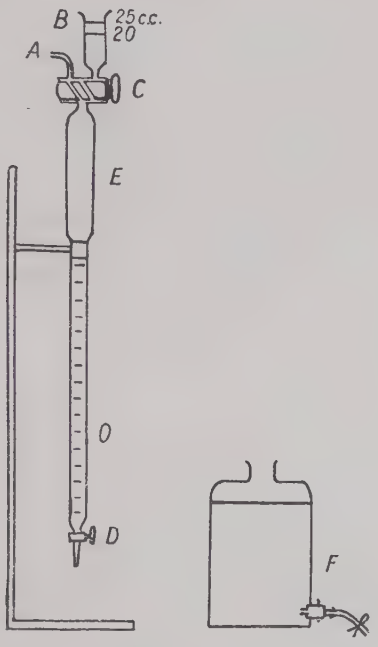


FIG. 11.

Attach the aspirator tube, filled with water, to the lower end of the burette, open the tap D and allow water to enter the burette until the level is slightly above O. Close the tap D.

(It is important in many operations for which the burette is employed that the tube of the aspirator should be completely filled with water before it is attached to the burette, or air will be introduced.)

The air in the burette is thus slightly compressed. Remove the aspirator tube, open the tap D cautiously and allow

the level of the water in the burette to fall to O. The burette now contains 100 c.c. of air under a pressure which is still slightly greater than that of the atmosphere. Open the tap C, *so that E is in connection with B*. One or more bubbles of air pass through the water in the cup B, and the burette now contains 100 c.c. of air under atmospheric pressure *plus* the pressure of the small column of water in the cup B.

The reason for measuring the air in this way is that, after absorption of the oxygen from the air, the nitrogen is measured between similar columns of water, for reasons which will be apparent later.

Absorption of Oxygen.

Attach the lower end of the burette to a water pump, which is turned on slightly. Open the tap D very cautiously and allow the level of the water in the burette to fall nearly to the tap D.

Place 2·5 c.c. of a solution of pyrogallol (containing 30 gms. of pyrogallol in 100 c.c. of water) in a small porcelain basin; place the lower end of the burette in the solution, and by opening the tap D cautiously, allow most of the solution to enter the burette. Take care that no air is allowed to enter the burette.

In the same basin place approximately 15 c.c. of a solution of potassium hydroxide (containing 150 gms. of commercial caustic potash in 100 c.c. of water) and allow as much as possible of this solution to enter the burette as before. Close the tap D and pour out the water from the cup B. Support the burette in a horizontal position, and keep the liquid inside in gentle motion for the next five minutes.

A considerable reduction of pressure will be effected during the absorption of the oxygen, and it is very important that no leakage of air into the burette should take place.

At the end of five minutes support the burette vertically and fill the cup B with water. Open the tap *C* slightly, so that *the cup B is in connection with E*. Allow water to run into B as fast as it runs into the burette.

When no more water enters the burette, open the tap D over the sink, and again allow water to run into the cup B until all the coloured liquid has been washed out of the burette. For this purpose a convenient arrangement is to have a piece of glass tube, bent twice at right angles, and attached to a water tap by means of a long length of rubber tubing, one end

of this glass tube being placed in the cup of the burette. It is essential to keep water in the cup B while liquid is running out from the tap D.

When all the pyrogallol-potash mixture has been washed out from the burette, close the tap D and remove the glass tube from the cup B. Open the tap D slightly, and allow the water in the cup B to fall to the original level, i.e. the 25 c.c. or 20 c.c. mark. Close the tap D when this is the case, and allow the burette to drain for a few minutes.

Read off the level of the water in the burette. The reading gives the volume of oxygen in 100 c.c. of air taken for the experiment, since both gases are measured under the same conditions of temperature and pressure.

Repeat the whole experiment.

On the average, fresh air contains approximately 21·0 per cent. of oxygen by volume.

From the point of view of Hygiene, the determination of the percentage of oxygen in the air is of considerably less importance than the determination of water vapour, carbon dioxide and other substances which are present in very small quantities.

DETERMINATION OF OXYGEN BY MEANS OF THE HEMPEL APPARATUS.

The complete apparatus, Fig. 12, consists of a burette A and several absorption pipettes of the type B and C.

The burette consists of two tubes joined by means of a length of rubber tubing,* and supported vertically by means of wooden stands. One of the tubes is graduated in fifths of a cubic centimetre from 0 to 100 c.c.

The upper end of the graduated or measuring tube is fitted with a short length of pressure tubing carrying a good screw clip, L, and fitted with a short length of thick walled glass tubing about 1 mm. internal diameter, bent twice at right angles. The other tube of the burette is usually referred to as the pressure tube.

Method of Filling Hempel Pipettes.

The absorption pipettes are either single, as shown in B, or double as in C. The advantage of the latter form of pipette

* It will be found convenient to have this rubber tube divided in the middle, and the ends joined by means of a piece of glass tubing carrying a glass stop-cock K.

is that the absorbent in D and E is kept out of contact with the atmosphere, by means of water placed in the bulbs F and G.

The capillary tubes of the pipettes are fitted with short lengths of pressure tubing which are securely wired on and carry good screw clips. When not in use, the capillary end of the pipette is closed by means of a short length of glass rod, fitted into the pressure tube, and the other end of the pipette is closed by means of a small cork.

For the absorption of oxygen a double pipette containing

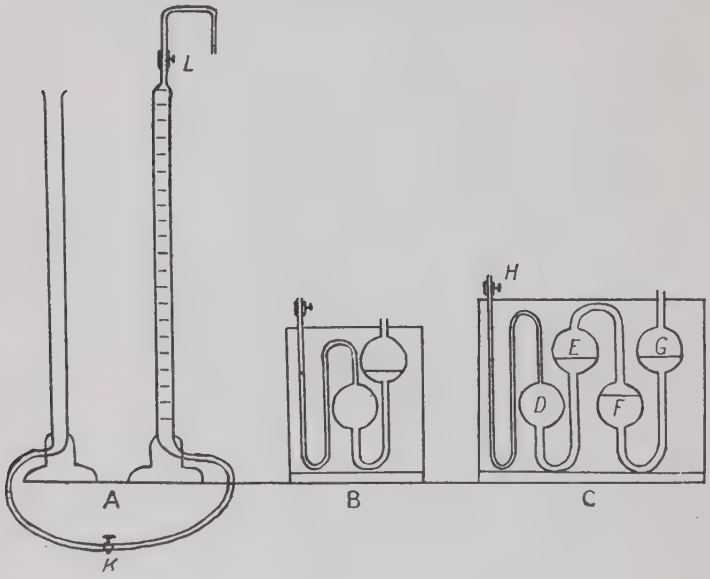


FIG. 12.

a solution of sodium hydrosulphite, or pyrogallol and potash is required. The solution of hydrosulphite employed contains 25 gms. of sodium hydrosulphite (hyposulphite) and 15 gms. of sodium hydroxide in 135 c.c. of water.*

A double absorption pipette is filled by first inverting it, and attaching an ordinary 10 c.c. pipette to its capillary end.

The lower end of the ordinary pipette dips into a vessel containing the absorbent.

A water pump is attached to the open end of the absorption pipette and liquid is drawn in until the bulb D is filled.

* Oxygen is absorbed by the hydrosulphite according to the equation

$$Na_2S_2O_4 + H_2O + O_2 \rightarrow NaHSO_3 + NaHSO_4.$$

The absorption pipette is now placed in an upright position, the 10 c.c. pipette still being attached and full of the absorbent.

The liquid is allowed to flow into the absorption pipette until a small amount is contained in the bulb E.

Some water is poured into the bulb G and is transferred to the bulb F by applying a water pump to the end of G. Care should be taken that the liquid in the bulb E does not pass over into the bulb F.

The absorbing liquid is drawn nearly to the top of the capillary tube of the pipette by means of the water pump, and the clip on the pressure tube H is closed.

A single pipette may be filled by pouring the liquid through a funnel in the wide tube of the pipette, and drawing the liquid nearly to the top of the capillary tube by means of a water pump.

Sample of Air for Analysis.

Pour water into the pressure tube of the burette, and fill the measuring tube with water, by raising the pressure tube and opening the tap K and the clip L. When this tube is full close the tap K. The pressure tube should now contain only a small quantity of water.

Draw a sample of air into the measuring tube by opening the tap K and lowering the pressure tube. Adjust the level of the water in the measuring tube until exactly 100 c.c. of air is contained in the tube, when the levels of the water in the measuring and pressure tubes are the same. The burette now contains 100 c.c. of air at atmospheric pressure.

Close the tap K and the clip L.

Open the tap K and make sure that the volume of air is exactly 100 c.c. when the level of the water in both tubes is the same.

Since the gas after absorption of any constituent is measured under the same conditions, that is, with the levels of the water in both tubes the same, the diminution in volume, produced by the absorption of that constituent, gives at once its percentage by volume in the gas under examination.

Absorption of Oxygen.

Support the double absorption pipette containing the solution of sodium hyposulphite* on a wooden stand, so that the end

* Or pyrogallol and potash.

of the bent glass tube, attached to the measuring tube of the burette, is at a slightly lower level than the upper end of the pressure tubing H, attached to the capillary of the absorption pipette.

Remove the air as far as possible from the pressure tubing H, by pressure between the fingers and thumb, and fit the glass tube attached to the burette securely into the pressure tubing H.

Open the clip on H and note the level of the liquid in the capillary tube.

Open the clip L, and by raising the pressure tube, drive the air into the absorption pipette, until the level of the water in the measuring tube reaches the clip L. Close the tap K and the clip on H.

Allow the gas to remain in contact with the absorbent for five minutes, shaking the pipette occasionally backwards and forwards.

At the end of the five minutes open the tap K and the clip on H, and allow the gas to pass back into the measuring tube, by lowering the pressure tube, until the liquid in the capillary of the absorption pipette is at the same point as before the absorption.

Close the tap K and the clip on H. Open the tap K and bring the water in the pressure and measuring tubes to the same level.

Read off the volume of the residual gas.

One hundred c.c. less this volume of gas gives the percentage of oxygen in the air under examination.

To ensure that the absorption of oxygen is complete, pass the gas again into the absorption pipette as before, and after allowing it to remain there for a few minutes, with occasional shaking, transfer it again to the measuring tube and read off the volume of the residual gas at atmospheric pressure.

It is, of course, essential to have the tap K (on the rubber tube joining the pressure and measuring tubes) open, when adjusting the levels of the water in the two tubes.

Repeat the experiment and compare the results obtained with those obtained by means of the Bunté apparatus,

DETERMINATION OF CARBON DIOXIDE AND OXYGEN IN EXPIRED AIR.

Method of Collecting the Sample of Expired Air.

Fit up a set of aspirators as shown in the diagram, Fig. 13.

Place both bottles on the bench, open the clips C and D and pour a saturated solution of common salt into A until both bottles are rather more than half filled.

Place the bottle A on a wooden stand and allow the solution to flow into B until this bottle is filled completely.

Close the clips C and D, and place the bottle B on the wooden stand as shown in the diagram.

Take a deep inspiration and hold the breath for a few seconds. Breathe out through the glass tube E, opening the clips D and C.

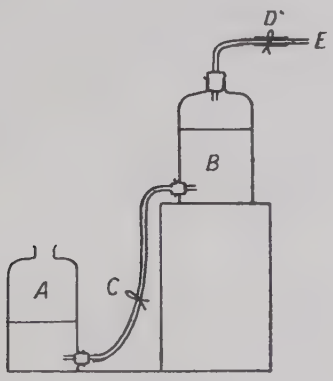


FIG. 13.

Close the clips and repeat the process until B is about three-quarters full of expired air. Place both bottles on the bench.

Fill the Bunté burette with salt solution, by placing the lower end in the solution and drawing out the air by means of a water pump attached to the gas inlet tube. Fill the cup of the burette with water up to the 20 c.c. or 25 c.c. mark.

Attach the gas inlet tube A of the burette to the rubber tube attached to the top of the aspirator bottle B. Open the clips of the aspirator and the taps of the burette. Raise the aspirator bottle A and allow expired air to pass into the burette until rather more than 100 c.c. has been collected. Close the taps of the burette and the clips of the aspirator.

Adjust the volume of expired air in the burette until exactly 100 c.c. is obtained under atmospheric pressure plus the pressure due to the column of water in the cup of the burette (see p. 189).

The carbon dioxide must obviously be absorbed before the oxygen, as the solution of pyrogallol and potassium hydroxide would absorb both this gas and oxygen.

Carbon Dioxide.—For the absorption of the carbon dioxide 15 c.c. of a solution of potassium hydroxide (containing 50 gms. of commercial caustic potash in 100 c.c. of water) is employed. See page 190 for method of introducing the absorbent.

After the absorption of the carbon dioxide, the solution of potassium hydroxide is washed out from the burette, and the diminution in volume of the gas gives the percentage of carbon dioxide in the expired air under examination.

Oxygen.—The oxygen in the gas remaining in the burette is now determined by absorption, as described on page 190.

The diminution in volume gives the percentage of oxygen in the expired air.

The percentage of carbon dioxide and oxygen in the sample of expired air should also be determined by means of the Hempel apparatus,* the carbon dioxide being absorbed in a Hempel pipette containing a solution of potassium hydroxide (120 gms. of potassium hydroxide in 500 c.c. of water). The oxygen in the gas remaining after the absorption of the carbon dioxide is determined as described on page 193. The diminution in volume, in each case, gives the percentage of the constituent absorbed, in the expired air.

For expired air collected as described above the percentage of carbon dioxide is usually about 4 per cent. and the oxygen 16 per cent. by volume.

DETERMINATION OF SULPHUR DIOXIDE AND SULPHURIC ACID IN AIR.

All fuels, solid, liquid and gaseous, contain compounds of sulphur in varying amounts as impurities. Thus ordinary bituminous coal contains from 0·5 to 3·5 per cent. of sulphur, largely present as iron pyrites. Coal gas contains organic compounds of sulphur, although during its manufacture a large

* For method of obtaining exactly 100 c.c. of the gas at atmospheric pressure in the measuring tube see page 206.

proportion of the sulphur contained in the coal is removed.* Liquid fuels also invariably contain sulphur compounds, a circumstance which has to be taken into account in connection with their use for certain purposes. See "Chemistry of Petroleum," by Tinkler and Challenger.

On the combustion of a fuel, a small quantity of the sulphur may escape as sulphuretted hydrogen, but most of it is converted by combustion into sulphur dioxide, which escapes with the other products of combustion. This sulphur dioxide (or sulphurous acid) is rapidly oxidised to sulphuric acid.

The irritating effect on the mucous membrane of sulphurous acid in fog is well known, but it is the free sulphuric acid, produced by its oxidation, which is mainly responsible for the harmful effects on vegetation and masonry, and even for such minor effects as the breaking of picture cords in a house.

The tarnishing of copper and silver articles exposed to air, especially during a fog, is probably due to the presence of traces of sulphuretted hydrogen, and not to the sulphurous and sulphuric acids in the air.

One of the objections urged against the use of coal gas for illuminating purposes is the production of small quantities of sulphurous and sulphuric acids on its combustion. It has, however, been found by Hehner and Rideal that these acids are rapidly absorbed by the whitewash on the ceiling of an ordinary room.

(See Report of Conference on Heating and Lighting, London, Oct., 1913, p. 6.)

The determination of the amount of sulphurous and sulphuric acid in the air is carried out by drawing a measured volume of the air through a long glass tube, filled with glass beads moistened with a dilute solution of hydrogen peroxide, whereby the sulphurous acid is oxidised to sulphuric acid. This acid, together with the sulphuric acid originally present in the air, remains in the solution, and its amount is determined in the ordinary way by precipitation as barium sulphate. Since the amount of this substance obtained is usually very small, a special centrifugal method, which does not involve filtration, is often adopted for its determination.

The apparatus employed for the determination is shown in the diagram Fig. 14.

* See p. 212 for determination of "sulphur" in coal gas.

A very dilute solution of hydrogen peroxide (2 c.c. of a 10 volume solution, free from sulphate, in 250 c.c. of water) is allowed to flow, at a rate of about one drop per second, from the tap funnel A on to the glass beads contained in the tube B, which is about 1 metre long and 2 cm. diameter.

The air to be examined enters through the lower side tube, a glass tube leading to the outside air being attached to C. The upper side tube D is attached to a meter, and air is drawn

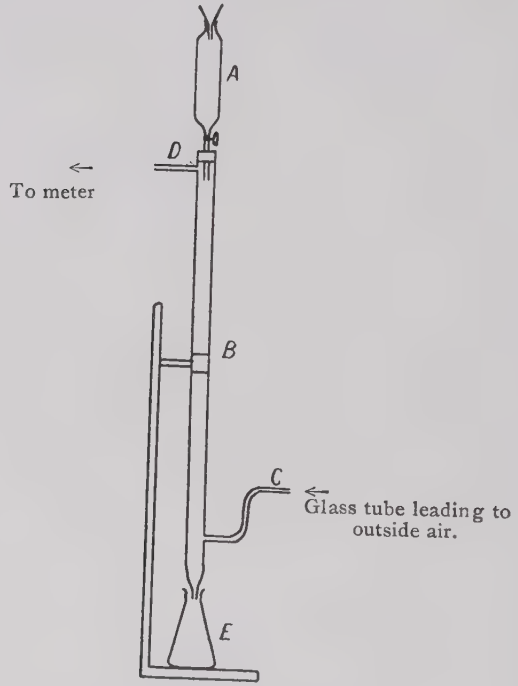


FIG. 14.

through the apparatus by connecting the outlet tube of the meter to a water pump, or by an arrangement which enables the wheel of the meter to be driven by means of a falling weight. See "Smoke," by Cohen and Ruston (Arnold).

The rate at which the air is drawn through the meter is about 20 cub. ft. (566 litres) per hour. A meter suitable for this purpose is shown in Fig. 30. When nearly all the liquid has dropped from the funnel A, the contents of the flask E are poured back into A, so that a constant stream of liquid

is passing over the beads during the whole of the experiment. The drop of liquid in the lower end of B prevents access of air to the tube B except through C.

At least 3 cubic metres of air should be drawn through the apparatus, unless the amount of sulphurous and sulphuric acids is likely to be high as in the case of a fog.

After a measured volume of air has been freed from these acids, the whole of the liquid is collected in the flask E, and the funnel and beads washed by means of distilled water, the washings being allowed to collect in E. The very dilute solution of sulphuric acid contained in this flask is neutralised, evaporated to a very small bulk and transferred to a small uncorked, weighed test tube (about 7·5 × 1·5 cms.), the vessel being washed out with successive small quantities of distilled water. A small quantity of ammonium chloride solution is added, and the solution heated nearly to boiling. A few drops of a hot solution of barium chloride are then added and the tube, after fitting with a rubber bung, is placed in an upright position and allowed to stand for some hours. It is then put in a centrifuge and whirled at a high speed for five minutes. The test tube should be placed inside a thick-walled glass tube containing a plug of cotton wool at the bottom, and a similar tube containing a test tube filled with water should be employed as a counterpoise in the centrifuge.

The treatment in the centrifuge is repeated until the solution is no longer turbid. When this is the case, the liquid is carefully siphoned off by means of a thin glass tube bent twice at right angles. Hot distilled water is added and the tube again placed in the centrifuge. When the liquid is quite clear, it is siphoned off and the process of washing is repeated until the liquid is free from chloride. The liquid is then finally siphoned off, and the tube dried in the steam oven until the weight is constant.

From the increase in weight of the tube, the amount of barium sulphate, and hence of sulphuric acid is found. This is the sulphuric acid and sulphurous acid, expressed sulphuric acid, in the volume of air drawn through the apparatus.

The result should be expressed as mg. H_2SO_4 per 100 cub. ft. of air. These results, as would be expected, vary very considerably, both according to the locality where the air is examined, and to the weather prevailing at the time of the experiment.

With country air in fine weather the amount is usually

less than 1 mg. per 100 cub. ft., whereas in the centre of a town during fog as much as 30 mg. per 100 cub. ft. may be found.

For further information on this subject see "Smoke," by Cohen and Ruston (Arnold), and article on "Smoke and Smoke Prevention," "Thorpe's Dictionary of Applied Chemistry," Vol. IV.

For methods employed for the determination of hydrogen peroxide, ozone, ammonia, nitrous and nitric acids in air, see "Technical Methods of Chemical Analysis," G. Lunge, C. A. Keane, Vol. I.

For determination of carbon monoxide in air due to the incomplete combustion of coal gas, see page 231.

The importance of even minute quantities of impurities in air will be recognised when it is remembered that, whilst the amount of solid food and water consumed by an adult are approximately 2·5 and 4·5 lb. respectively per day, the amount of air inhaled is about 30 lb. per day.

DETERMINATION OF THE AMOUNT OF SUSPENDED MATTER IN AIR.

This determination is carried out by drawing a measured volume of air through a weighed plug of cotton wool, which retains the suspended matter.

The cotton wool is contained in a thin glass tube, made by drawing out a test tube about 1·5 cms. in diameter, so as to form a funnel. This glass tube is supported inside a wider metal tube, which is placed in the aperture of a window.

Before the experiment is started, the glass tube containing the cotton wool is dried in the steam oven, and whilst it is cooling, before weighing, a slow stream of air is drawn through by means of a water pump, to prevent condensation of moisture. The drying is repeated until the weight is constant.

The tube is then attached to a meter connected with a water pump, and a current of air drawn through the plug. The rate at which the air passes through should be about 200 litres per hour.

After a considerable volume of air has been drawn through the plug, the increase in weight of the latter is determined, after drying in the steam oven, as described above.

The result should be expressed as mg. of suspended matter per 100 cub. ft. of air.

The amount so found varies very considerably according to the place at which the experiment is carried out, and the weather conditions prevailing at the time of the experiment.

For other methods employed for this determination see Lunge, Keane, Vol. I., Part II.

The question of suspended matter in the air is of importance in connection with the question of fuel economy. It has been estimated, for example, that 54,000 tons of solid matter were deposited from the air in the county of London in the year 1916, most of which represented fuel lost in the form of smoke.

For further information on this subject see "Smoke," by Cohen and Ruston, and Report on Atmospheric Pollution, "The Lancet," 27 October, 1917.

EXAMINATION OF THE EFFICIENCY OF THE VENTILATION OF A GIVEN ROOM.

Although it is now generally recognised that carbon dioxide, as such, is not injurious in quantities in which it is likely to be present, even in the air of an ill-ventilated, crowded room, the proportion of this gas present in the air of a room affords an indication of the amount of other impurities produced by respiration. On account of the ease with which the quantity of carbon dioxide may be determined, and the difficulty of determining the amount of the organic substances which accompany it, the determination of the proportion of carbon dioxide in the air of a room is still one of the best means of investigating the efficiency of the ventilation of the room. The methods employed for the determination have previously been described.

In addition to the amount of carbon dioxide in the air, the relative humidity and the advisability of the air being in motion, to facilitate evaporation from the surface of the skin, are also points of great importance in this connection.

The amount of carbon dioxide produced by an adult at rest is approximately 0·6 cub. ft. per hour. This is calculated as follows:—

Sixteen respirations, each of 30 cub. ins., per minute give $16 \times 30 \times 60 = 28{,}800$ cub. ins. of expired air per hour.

Four per cent. of this, 1152 cub. ins., or 0·6 cub. ft., is carbon dioxide.

Not only is the carbon dioxide content of the air of a

room increased by respiration, but the amount of water vapour in the air will also be raised, since expired air is saturated with moisture.

The amount of carbon dioxide normally present in fresh air is approximately 0·04 per cent., and it is generally agreed that the amount of this substance in the air of a room should not at any time exceed 0·06 per cent., an increase of 0·02 per cent. above the normal amount for fresh air.

It is therefore necessary to calculate how much fresh air per hour is required to dilute the products of respiration, in order that the carbon dioxide content of the air of a given room shall not rise above 0·06 per cent., and also to be able to measure the amount of air which is entering the room through any given aperture. This is measured approximately by means of an anemometer (see below).

It is also necessary in this connection to measure the cubical contents of a given room. This is accomplished by applying the ordinary rules of mensuration, deducting from the product of the three dimensions of the room the volume of any large solid objects.

THE MEASUREMENT OF AIR CURRENTS BY MEANS OF THE ANEMOMETER.

One form of this instrument is shown in the diagram, Fig. 15.

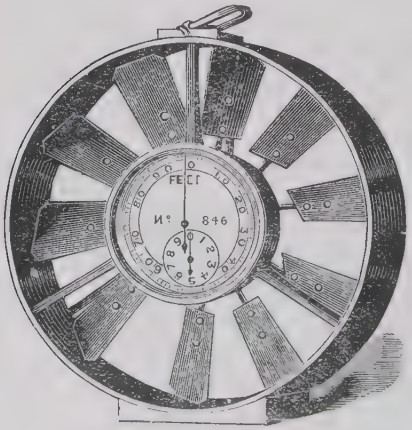


Fig. 15.—Anemometer.

It consists of a number of blades attached to an axle, which is very delicately mounted, and which is connected by means of an endless screw with a set of dials. The instrument is so graduated that the change in the reading indicated by the dials, in one minute, when the instrument is in use, gives the velocity of the air current in feet per minute.

The recording mechanism of the instrument can be started and stopped at will, so

that in measuring a given air current, after noting the readings registered by the dials with the recording mechanism stopped, the blades are allowed to attain their maximum rate of revolution before the recording mechanism is started.

At the end of one minute the recording mechanism is stopped, and the change in the reading of the dials gives the velocity of the given air current in feet per minute.

A determination should be made by means of the instrument, for example, of the amount of air which is entering a room through the lower sash of a window, or if this is acting as an outlet, owing to the direction of the wind, the amount of air passing out through this opening should be determined.

Owing to the fact that the velocity of the air is different in different parts of the aperture, readings should be taken near the top, in the middle, and near the bottom of the opening. The average result is taken as the velocity of the air through the window.

This velocity in feet per minute × the area of the aperture × 60, gives the amount of air in cubic feet per hour entering or leaving the room through this opening.

In the same way the amount of air entering or leaving the room by any other aperture may be found.

It will be understood that only an approximate idea of the amount of air entering or leaving a room can be obtained by means of the anemometer.

It is difficult, for example, to measure the amount of air which enters a room under the door, which is often the chief means of access of fresh air to a room.

From the measurement of the cubical contents of a room, and the amount of air which is entering or leaving the room per hour, a calculation should be made of the number of times per hour the air of a room is being changed.

It is generally agreed that three times per hour is usually the maximum number of changes of the air of a room, which can be borne with comfort in this country, although with a coal fire, the amount of air passing up the chimney often gives a value which is probably greatly in excess of this.

CALCULATIONS RELATING TO THE CARBON DIOXIDE CONTENT OF THE AIR OF A ROOM.

1. If the initial air space per person in a room is 1000 cub. ft., which is a suitable standard, what amount of fresh air

per hour is required to dilute the products of respiration of each person, so that the carbon dioxide content does not rise above 0·06 per cent.?

0·06 per cent. of CO_2 corresponds to 0·0006 cub. ft. CO_2 in 1 cub. ft. of air, an increase of 0·0002 cub. ft. of CO_2 over the amount normally present in fresh air.

∴ 0·0002 cub. ft. CO_2 is the excess allowable in 1 cub. ft. of air.

∴ 0·6 cub. ft. CO_2 (the amount produced per person per hour) is the excess allowable in

$$\frac{1 \times 0{\cdot}6}{0{\cdot}0002} = 3000 \text{ cub. ft. of air.}$$

Hence 3000 cub. ft. of fresh air per hour are required to dilute the products of respiration from one person; but if the initial air space per person is 1000 cub. ft., the amount of fresh air required per hour per person is 2000 cub. ft. The result might also be stated as follows: One person produces in one hour sufficient carbon dioxide to raise the percentage of this substance in 3000 cub. ft. of air from 0·04 to 0·06.

2. The carbon dioxide content of the air of a room 10 × 10 × 20 ft. after occupation by two persons for one hour is found to be 0·09 per cent. What volume of fresh air has been admitted to the room during the period of occupation?

Assuming that the CO_2 content of the air of the room before occupation was 0·04 per cent., the carbon dioxide due to respiration is 0·09 − 0·04 = 0·05 per cent.

Amount of carbon dioxide produced by respiration by two persons in one hour = 0·6 × 2 = 1·2 cub. ft.

Since the air of the room after occupation contains 0·05 per cent. CO_2 due to respiration, 0·0005 cub. ft. CO_2 produced by respiration is distributed through 1 cub. ft. of air.

∴ 1·2 cub. ft. CO_2 are distributed through $\frac{1 \times 1{\cdot}2}{0{\cdot}0005}$ = 2400 cub. ft. of air.

Volume of air in the room = 10 × 10 × 20 = 2000 cub. ft.

∴ 2400 − 2000 = 400 cub. ft. of fresh air have been supplied during the hour the room was occupied.

3. If two persons occupy a room of 2000 cub. ft. for three hours, and 1000 cub. ft. of fresh air per hour are supplied, what will be the percentage of carbon dioxide in the air of the room at the end of the period of occupation?

In this case 0·6 × 2 × 3 = 3·6 cub. ft. CO_2 are distributed

through 2000 + 3000 = 5000 cub. ft. of air, so that the air contains 0·072 per cent. CO_2 due to respiration. This carbon dioxide with the 0·04 per cent. normally present in fresh air gives a total percentage of 0·112.

4. If two persons occupy a room of 2000 cub. ft. for eight hours, what volume of fresh air per hour should be supplied, in order that the carbon dioxide content of the air shall not exceed 0·06 per cent.?

Carbon dioxide produced by respiration during occupation of room, $0{\cdot}6 \times 8 \times 2 = 9{\cdot}6$ cub. ft.

In order that the carbon dioxide content (due to respiration together with that normally present in the air) shall not exceed 0·06 per cent., 0·0002 cub. ft. CO_2 due to respiration is to be distributed in 1 cub. ft. of air.

$\therefore$ 9·6 cub. ft. CO_2 distributed in $\frac{9{\cdot}6}{0{\cdot}0002}$ cub. ft. of air

= 48,000 cub. ft. of air.

Air originally present = 2000 cub. ft.

$\therefore$ 46,000 cub. ft. of air must be added during the eight hours

= 5750 cub. ft. per hour.

It will be noticed that it is assumed in the above calculations that the fresh air is supplied at a constant rate. This is unlikely to be the case, however, with any system of natural ventilation owing to changes in the direction of the wind, etc.

Chapter VIII.

GASEOUS FUELS.

An outline of the methods employed in the manufacture of coal gas, producer gas, water gas, carburetted water gas, etc., is given in the lectures.

In connection with this subject see articles on "Fuel" and "Gas," Thorpe's "Dictionary of Applied Chemistry" (Longmans).

ANALYSIS OF COAL GAS BY MEANS OF THE HEMPEL APPARATUS.

Fill the measuring tube of the Hempel burette (Fig. 12, A, p. 192) with water which has been saturated with coal gas. This saturation is accomplished by allowing a stream of the gas to pass for about two minutes through about 300 c.c. of water contained in a 500 c.c. bottle. The bottle is then stoppered and shaken for a few minutes.

Attach a rubber tube, from which coal gas is escaping, to the capillary tube attached at L (Fig. 12, A), open the tap K and the clip L, and allow rather more than 100 c.c. of coal gas to enter the measuring tube. Close the tap K and the clip L, and remove the gas supply tube. Open the tap K and by raising the pressure tube compress the gas in the measuring tube until its volume is exactly 100 c.c. Close the tap K and open the clip L momentarily, so as to allow the excess of gas to escape, and then make sure that exactly 100 c.c. of gas at atmospheric pressure are contained in the measuring tube, i.e. when the tap K is open and the levels of the water in the pressure and measuring tubes are the same.

The constituents of the coal gas are now to be absorbed in the following order:—

(1) Carbon dioxide by potassium hydroxide solution.

(2) Oxygen by sodium hydrosulphite or alkaline pyrogallate solution.

(3) Olefines and aromatic hydrocarbon vapours by fuming sulphuric acid.

(4) Carbon monoxide by an acid solution of cuprous chloride.

This leaves a gas consisting of a mixture of hydrogen, methane and nitrogen, the amounts of which are determined by explosion with air, as described on page 208.

The solutions required for the pipettes for the absorption of carbon dioxide and oxygen have been described previously.

The pipette filled with fuming sulphuric acid should be handled with great care on account of the strong corrosive action of the absorbent, and care must be taken that no water is allowed to enter the pipette through the capillary tube when the gas is being introduced.

Olefines are absorbed by fuming sulphuric acid owing to the formation of esters, e.g.—

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5HSO_4.$$

Benzene and its homologues are absorbed owing to the formation of sulphonic acids, e.g.—

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O.$$

The solution of cuprous chloride for the absorption of carbon monoxide contains 30 gms. of cuprous chloride dissolved in 50 c.c. of water and 150 c.c. of concentrated hydrochloric acid. A few strips of copper foil should be added when the solution is made up. Owing to the action of the oxygen of the air on the reagent, a double Hempel pipette should be employed for this solution.

Cuprous chloride absorbs carbon monoxide owing to the formation of an unstable compound, $Cu_2Cl_2 . CO$.

The transference of the gas from the burette to a pipette is carried out as described on page 193.

If 100 c.c. of gas are taken, the diminution in volume, after absorption of any constituent, gives at once the percentage of that constituent in the original coal gas.

It is important to remember that the gas in the measuring tube after absorption of any constituent must be measured at atmospheric pressure. That is, the clip L must be closed, the tap K open, and the levels of the water in the pressure and measuring tubes must be the same.

It should also be noted that it is often advisable to pass the gas into contact with the reagent in a pipette a second

time, in order to ensure complete absorption. This is especially the case in the absorption of carbon monoxide, or in the case of a reagent which has been in use for some time.

Example :—

100 c.c. of coal gas.
Volume after absorption of carbon dioxide = 98·6
Per cent. of carbon dioxide = 1·4.
Volume after absorption of oxygen = 98·2
Per cent. of oxygen = 98·6 − 98·2 = 0·4.
Volume after absorption of olefines and vapours of aromatic hydrocarbons = 93.
Per cent. of olefines, etc., 98·2 − 93 = 5·2.
Volume after absorption of carbon monoxide = 84·0 c.c.
Per cent. of carbon monoxide = 93 − 84 = 9·0.

Determination of Methane and Hydrogen.

The gas remaining after the absorption of the carbon monoxide consists of hydrogen, methane and nitrogen, for

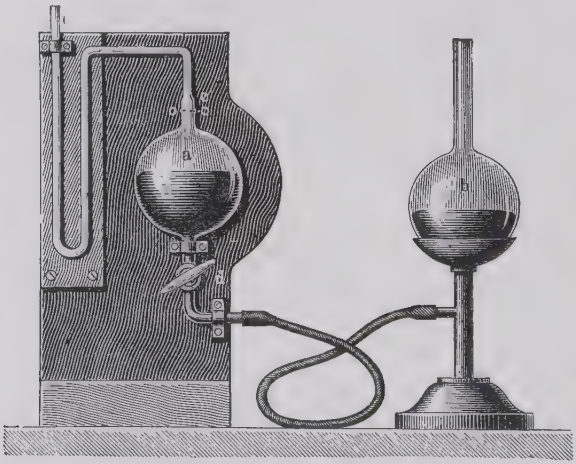


Fig. 16.—Explosion Pipette.

the determination of the amounts of which an *explosion pipette*, Fig. 16, may be employed.

In this pipette the bulb *a* has two platinum wires *c*, fused into the glass, by means of which a spark discharge can be passed through the gas contained in the bulb. The bulb *a* is

also fitted with a stop-cock *d*, and is connected to the bulb *b* by means of pressure tubing.

By opening the stop-cock and raising the bulb *b*, the bulb *a* and its capillary tube are completely filled with mercury,* which is the confining liquid in this case. The pipette is now ready for use.

The capillary tube is fitted with a short length of pressure tubing, fastened on with wire and carrying a good screw clip.

Explosion of the mixture of hydrogen, methane and nitrogen with air, gives rise to water and carbon dioxide, the nitrogen remaining unchanged mixed with the excess of air.

From the contraction observed on explosion and the volume of carbon dioxide produced, the amounts of methane and hydrogen are determined as follows:—

From the equation

(1) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 vol. + 2 vols. → 1 vol.

3 vols. → 1 vol. (a contraction of two volumes)

it will be seen that the volume of methane is equal to the volume of carbon dioxide produced by its combustion.

Oxygen is used both for the combustion of the methane and for the hydrogen, the combustion of which takes place according to the equation,

(2) $2H_2 + O_2 \rightarrow 2H_2O$

2 vols. 1 vol. → no appreciable volume.

3 vols.

The water which is produced in both cases occupies no appreciable volume, since it condenses.

It will be seen, therefore, that the contraction in volume which takes place owing to the combustion of the methane, must be twice the volume of the methane present, since *one* volume of methane and *two* volumes of oxygen give only *one* volume of carbon dioxide (Equation 1).

The total contraction on explosion is measured.

The volume of methane is equal to the volume of carbon dioxide produced, which is determined by absorption by potassium hydroxide solution; so that the total contraction

* This explosion pipette should always be used over a mercury tray.

on explosion *minus* twice the volume of carbon dioxide produced from the methane, gives the contraction due to the combustion of the hydrogen. That is, the total contraction *minus* the contraction due to the combustion of the methane, equals the contraction due to the combustion of the hydrogen.

From equation (2) it will be seen that as a result of the combustion of the hydrogen three volumes of gas disappear, of which two volumes are hydrogen, or $\frac{2}{3}$ the contraction due to the combustion of the hydrogen is hydrogen.

Owing to the fact that a large excess of air must be mixed with the gas before explosion, it is not possible to use the whole of the residual gas after absorption of the carbon monoxide for the determination of hydrogen and methane.

After the absorption of the carbon monoxide transfer the gas, with the exception of about 15 c.c., from the burette to the pipette containing cuprous chloride solution. The gas in this pipette may be used if a second determination of the hydrogen and methane should be necessary.

Close the clip L, attached to the measuring tube of the burette, and measure the volume of gas now contained in the tube, with the tap K open, and the water in the pressure and measuring tubes at the same level. Lower the pressure tube below the level of the bench, open the tap K and the clip L at the top of the measuring tube and allow air to enter until the total volume of the gas is about 95 c.c.

Take care that none of the gas originally in the measuring tube escapes during the admission of the air.

Close the clip L and measure the total volume of gas in the measuring tube.

Transfer the whole of the mixture to the explosion pipette, and by lowering the bulb *b*, reduce the pressure in the bulb *a* of this pipette, in order to diminish the force of the explosion. Close the clip on the pressure tubing attached to the capillary tube of the explosion pipette, and the stop-cock *d* attached to the bulb *a*.

Pass a spark through the gas by means of an induction coil, and notice if a flash is apparent when the spark is passed.

Transfer the gas to the measuring tube of the burette and measure the residual volume.

The original volume (hydrogen + methane + nitrogen + air) minus volume after explosion = total contraction.

Transfer the gas to a pipette containing potassium hydrox-

ide solution, allow it to remain in the pipette for five minutes, transfer to the measuring tube and note the diminution in volume, due to the absorption of carbon dioxide. This gives the volume of carbon dioxide produced by the combustion of the methane, and hence the methane in the volume of "residual" gas taken for the determination.

Calculate the volume of methane which would be contained in the total volume of gas left after absorption of the carbon monoxide. This will give the percentage of methane in the original coal gas.

Find the contraction due to the combustion of the hydrogen, by deducting twice the volume of carbon dioxide produced by the combustion of the methane from the total contraction observed on explosion.

Two-thirds of this contraction, due to the combustion of the hydrogen, is the volume of hydrogen in the volume of "residual" gas taken for the experiment.

Calculate the amount of hydrogen which would be present in the whole of the residual gas after absorption of the carbon monoxide. This gives the percentage of hydrogen in the original coal gas. The sum of the percentages of all the constituents which have now been determined deducted from 100 gives the percentage of nitrogen in the gas.

Example:—

Volume of gas after absorption of carbon dioxide, oxygen, olefines, etc., and carbon monoxide from 100 c.c. of coal gas = 84·0 c.c. "residual" gas.

Volume of this gas taken for analysis = 15·0 c.c.

„ „ „ „ + air „ „ = 95·2 „

„ „ gas after explosion = 71·6 c.c.

∴ Total contraction on explosion = 95·2 − 71·6

= 23·6 c.c.

After absorption of the carbon dioxide produced by combustion of the methane the volume = 65·4 c.c.

Volume of CO_2 = 71·6 − 65·4

= 6·2 c.c.

∴ 6·2 c.c. of methane were present in 15 c.c. of the "residual" gas.

15 c.c. "residual" gas contained 6·2 c.c. methane.

∴ 84 c.c. "residual" gas contained $\frac{6{\cdot}2 \times 84}{15}$ = 34·7 c.c.

$\therefore$ 100 c.c. original coal gas contained 34·7 c.c. of methane.

The contraction due to the combustion of the hydrogen = total contraction – the contraction due to the combustion of the methane (i.e. twice the volume of CO_2 from the CH_4)

$$= 23{\cdot}6 - 12{\cdot}4$$
$$= 11{\cdot}2 \text{ c.c.}$$

Two-thirds of this is hydrogen, i.e. $\frac{2}{3} \times 11{\cdot}2 = 7{\cdot}5$ c.c.

$\therefore$ 15 c.c. of "residual" gas contained 7·5 c.c. of hydrogen.

$\therefore$ 84 c.c. contained $\frac{7{\cdot}5 \times 84}{15} = 42{\cdot}0$ c.c.

or per cent. of hydrogen in original coal gas = 42.

Summary :—

100 c.c. of coal gas contained	1·4 c.c.	CO_2
	0·4 ,,	O_2
	5·2 ,,	olefines, etc.
	9·0 ,,	CO
	34·7 ,,	CH_4
	42·0 ,,	H_2
	92·7	

$\therefore$ per cent. of nitrogen in the coal gas = 100 – 92·7
= 7·3.

Assuming that the olefines, etc., are present only as ethylene, C_2H_4, calculate the volume of *air* required for the complete combustion of one volume of coal gas of which the composition is as above.

Determination of "Sulphur" in Coal-gas.

Coal gas does not contain free sulphur, but compounds of sulphur such as thiophene, C_4H_4S, are invariably present in the gas. In view of the fact that these sulphur compounds, on combustion, give rise to sulphurous and then sulphuric acid, their presence in coal gas is a matter of some importance from the point of view of Hygiene. Sulphuretted hydrogen should not be present in coal gas. This substance is tested for by passing the gas over filter paper moistened with a solution of lead acetate, when no darkening due to the formation of lead sulphide should be observed. (See "Notification of the Gas Referees," 1918, p. 7.)

For the method employed for the determination of the total "sulphur" in coal gas, see "Chemistry of Petroleum," by Tinkler and Challenger, p. 169, and "Notification of the Gas Referees," 1918, p. 7.

THE USE OF COAL GAS FOR LIGHTING AND HEATING PURPOSES.

GAS BURNERS.

Flat Flame Gas Burners.

In a fish-tail burner, the construction of which is shown in the diagram (Fig. 17, A), the gas passes through cotton gauze, and at the top of the burner two jets of burning gas are made to impinge on one another. This may be illustrated by two small gas flames burning at the ends of glass tubes drawn out to fine jets. It will be noted that the flame of the gas burning at the open jet is quite unsuitable for purposes of illumination, but that when the jets impinge on one another, the shape of the flame, produced in a plane at right angles to that of the two jets, approximates to that obtained with an ordinary fish-tail burner.

In the batswing burner the gas issues from a fine slit, and the so-called Eureka economiser is constructed on the same principle.

For purposes of illumination these flat flame burners are quite unsuitable for the combustion of coal gas as now supplied, owing to the low natural luminosity of the gas. This is especially the case now that benzene and toluene vapours are being removed from the coal gas.

It should be noted, however, that the amount of *heat radiated* from such flames is considerably greater (about one and a half times) than that from the flame of a Bunsen burner consuming the same amount of gas, although, of course, the total amount of heat produced by the combustion of a given quantity of gas is quite independent of the type of flame produced, provided that combustion is complete.

The effect of the presence of benzene vapour on the luminosity of coal gas may be illustrated by means of the apparatus shown in the diagram, Fig. 17, B.

In this apparatus the glass tubes C and D are packed loosely with cotton wool.

Batswing or fish-tail burners are attached to C and D at the

upper ends, and the gas is supplied to the apparatus by means of a T tube.

When flames of equal size have been obtained, by regulating the screw clips E and F, the gas is turned off and the rubber bung at the upper end of one of the tubes C or D is removed. A few drops of benzene, C_6H_6, are then allowed to drop on the cotton wool in this tube. On re-lighting the gas jets, it

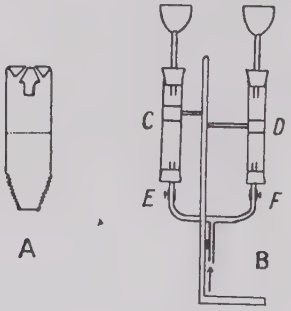


FIG. 17.

will be found that the gas containing the benzene vapour burns with increased luminosity.

Conversely, coal gas which is passed through absorption towers containing pumice moistened with fuming sulphuric acid (see p. 207), is entirely devoid of odour, and burns with a practically non-luminous flame.

It should be noted that the removal of benzene, toluene, etc., from coal gas causes a diminution of the calorific power as well as of the illuminating power of the gas.

The Bunsen Flame.

It is well known that in the production of this flame, a certain amount of air is mixed with the coal gas before combustion is effected. This *primary* air (about two volumes of air to one volume of coal gas, see p. 216) is drawn in owing to the fact that the gas enters the burner through a fine hole, and consequently at a high velocity, thus causing a slight diminution of pressure near the air hole of the burner.

The construction of a Bunsen burner and its method of action is illustrated by means of the apparatus shown in the diagram, Fig. 18.

A is a glass tube about 3 ft. (100 cms.) long and 1 inch

(2·5 cms.) internal diameter. A glass tube, drawn out to a fine jet, serves to introduce the coal gas, and a movable cork is placed on this tube.

By sliding this cork up and down it is possible to regulate the amount of primary air introduced. When no primary air is admitted, it will be found that the gas burns at the top of the tube with a large, irregularly shaped, luminous flame.

By slowly lowering the cork on the gas inlet tube, air is allowed to mix with the gas, and the flame at the top of the tube A gradually assumes the appearance of an ordinary non-luminous Bunsen flame.

By diminishing the supply of gas, by means of a screw clip on the rubber gas supply tube, it will be noticed that the inner cone of the flame becomes smaller, and that when the ratio of gas to air in the tube A reaches a certain value, the flame strikes back and the gas burns at the inlet tube. When this happens the gas should be immediately turned off.

The explanation of this phenomenon is as follows: Partial combustion of the coal gas, due to the admission of the primary air, takes place at the surface of the inner cone of the flame C. In the region marked B there is a mixture of unburnt gas and primary air.

The inter-conal gas D consists of a mixture of carbon monoxide, hydrogen, carbon dioxide, water vapour and nitrogen. No free oxygen is present.

Complete combustion with the formation of carbon dioxide and water takes place at the *surface* of the outer cone E.

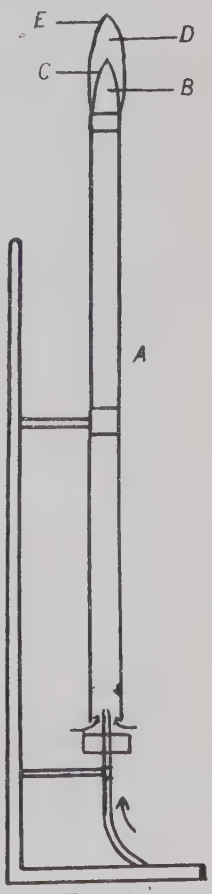


FIG. 18.

When the inner cone remains stationary, the velocity of the gaseous mixture issuing from the tube A, is equal to the initial rate of propagation of the combustion through the particular mixture of coal gas and air leaving the tube A. When, however, the amount of coal gas relative to the amount of air is diminished, a more explosive mixture is obtained and

the velocity of the mixture leaving the tube A is now less than the initial rate of propagation of combustion through the mixture; the explosion then travels down the tube and the gas burns at the inlet tube. The combustion, however, under these conditions is not complete, as is shown by the objectionable smell noticeable when a Bunsen burner "strikes back".

For example, the presence of acetylene, C_2H_2, in the products of this incomplete combustion may be shown by aspirating the products of combustion through a solution of cuprous chloride containing ammonia, when a red precipitate of cuprous carbide (or cuprous acetylide) is produced,

$$Cu_2Cl_2 + C_2H_2 \rightarrow Cu_2C_2 + 2HCl.$$

The experiment may also be carried out by simply holding an inverted gas jar for a few seconds over a Bunsen burner, which has been allowed to "strike back," and then shaking up the gas so collected with a solution of ammoniacal cuprous chloride.

If instead of a tube of uniform bore A, Fig. 18, a tube having a constriction near the top is employed, it is possible, by careful regulation of the supply of gas entering the tube, to arrest the descent of the inner cone at the constriction of the tube. The reason for this is that, at the constriction, the upward velocity of the gaseous mixture is greater than at the open end of the tube, and is also greater than the initial rate of propagation of the combustion through the gaseous mixture in the tube. This phenomenon of the separation of the two cones of a Bunsen flame is illustrated by means of the Smithells flame separator, see p. 217.

The phenomenon of "striking back" of a flame will also be illustrated by means of various lecture experiments.

The greatest amount of primary air which can be introduced into an ordinary Bunsen burner, without causing striking back, is about two volumes of air to one volume of coal gas, whereas for the complete combustion of coal gas the volume of air required is approximately five times that of the gas burnt. If, however, the burner be fitted with gauze to prevent striking back (see experiments with wire gauze, p. 218), the amount of primary air may be increased to the extent of three-fifths or four-fifths of the total amount of air required for combustion.

The Smithells Flame Separator.

The separation of the inner and outer cones of a Bunsen flame is well illustrated by means of this apparatus, the construction and mode of action of which is as follows :—

Two glass tubes of different diameters, one of which can be moved up and down inside the other, are joined by means of a piece of wide rubber tubing A, as shown in the diagram, Fig. 19. The inner tube is kept in a central position by means of a brass ring B. The open ends of both tubes are fitted with short lengths of metal foil.

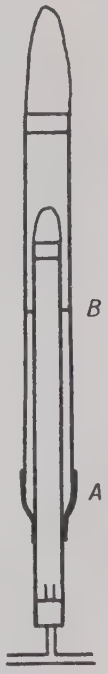


FIG. 19.

A mixture of coal gas and air is introduced into the inner tube by means of a T tube, one limb of which is attached to the gas supply, and the other to a supply of compressed air obtained by means of a water blower. The inner tube may, however, be attached directly to a Bunsen burner having a large hole for the admission of primary air.

The proportions of air and gas are then adjusted, so that the initial velocity of propagation of the flame, through the mixture entering the inner tube, is greater than the velocity of the gaseous mixture leaving the outer (wide) tube, but less than that of the mixture leaving the inner tube. When this is the case, the inner cone rests on the top of the inner tube, and the outer cone on the outer tube.

By means of a side tube the gas between the cones can be drawn off and its composition determined. It is found to consist of carbon monoxide, carbon dioxide, hydrogen, water vapour and nitrogen (from the primary air).

No free oxygen is present, so that no combustion is possible between the inner cone and the surface of the outer cone of a Bunsen flame.

The gaseous mixture, however, between the two cones is at a high temperature.

At the surface of the outer cone the carbon monoxide and hydrogen are completely oxidised to carbon dioxide and water.

Further Experiments to Illustrate the Structure of a Bunsen Flame.

It may be shown, by very simple experiments, that the combustion, due to the admission of primary air, takes place at the surface of the inner cone and not throughout the whole of this region.

1. A match supported vertically in the tube of a Bunsen burner by means of a pin, so that the head of the match is about 2 cms. above the end of the burner tube, is not ignited when the gas from the burner is lighted.

2. If a piece of cardboard, on which red mercuric iodide * has been rubbed, or a piece of asbestos paper, is placed for a few seconds (*a*) vertically in the flame, (*b*) horizontally in the inner cone of the flame, vertical and horizontal sections of the flame are obtained.

The colour change in the case of the asbestos paper is due to the carbonisation of the oil in the material.

Although combustion only takes place at the surface of the two cones, the portion between the two cones changes in colour owing to the high temperature of this region.

The Action of Wire Gauze in Arresting the Progress of a Flame.—This phenomenon, which is made use of in the construction of many types of gas burner, may be illustrated by placing two pieces of wire gauze, one above the other and about one inch apart, over an unlighted Bunsen burner. On turning on the gas this may be lighted (*a*) below the lower gauze and above the upper at the same time ; (*b*) between the two pieces of gauze only.

The explanation usually given is that, owing to conduction of heat by the gauze, the unburnt gas passing through is cooled below its ignition temperature.

It will be noticed in the experiments described above, that when the gauze becomes red hot, the flame usually passes through.

Incandescent Gas Burners.

The application of the Bunsen flame for purposes of illumination, in the so-called incandescent lighting by means

* Mercuric iodide (red) when heated is changed to a yellow modification of the substance. This yellow substance is, however, easily reconverted into the red modification simply by friction.

of upright and inverted burners, is well known. Numerous different types of both kinds of burners are in use. The main object is to get a flame of as high a temperature as possible, and to adjust the shape of the flame so that the mantle just fits on its outer edge. The higher the temperature of the mantle, the greater is the amount of light emitted by it.

Upright Incandescent Burners.

In the upright burners the gas passes through fine holes C in the base of the burner, Fig. 20, at a high velocity, which causes an inrush of primary air. The gas mixed with this air passes through a gauze or grid, which ensures proper admixture and prevents striking back (see p. 216).

If too much primary air is admitted, roaring is produced, and on most burners there is a simple device for diminishing the amount of primary air which is introduced.

To examine the construction of an upright incandescent burner, remove the mantle carefully from the mantle rod by means of a piece of wire or a long pin. The mantle is then suspended inside the lamp chimney.

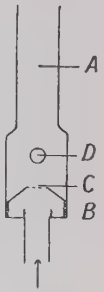


FIG. 20.

Remove the upper part of the burner which fits over the tube A. Unscrew the tube A at B, and clean out the small holes C by means of a pin. Note the primary air inlet holes D. Clean the gauze of the burner by means of a brush, after removing the mantle rod. Replace the burner and examine the flame. Turn off the gas, replace the mantle and adjust the supply of gas and primary air until the best light is obtained.

As much primary air as possible should be allowed to enter the burner, otherwise there is the possibility of a deposit of soot on the mantle.

It is, of course, a matter of common experience that a better light is often obtained with an incandescent burner when the gas supply is slightly reduced.

Inverted Incandescent Burners.

The chief advantage of the inverted burner is that the shadow of the burner is projected upwards, and not downwards as in the upright burner. One of the drawbacks to all

inverted incandescent gas burners, however, is that the hot products of combustion pass up over the burner, which is thereby corroded.

On the other hand, the mixture of gas and primary air in the burner is heated, thus effecting an economy of heat, as in the so-called regenerative burners.

In these inverted incandescent burners various devices are employed for regulating the gas and primary air supplies. Usually there is a fine adjustment for the gas supply, the construction of which is shown in the diagram, Fig. 21.

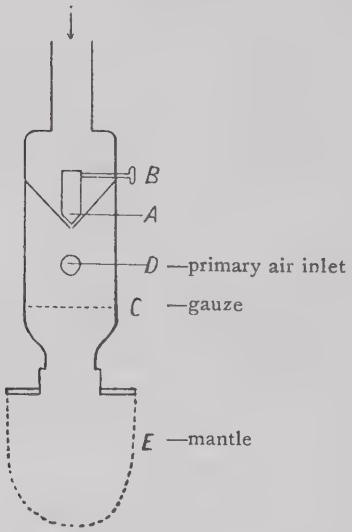


FIG. 21.

The plug A may be raised or lowered by means of a screw B. The primary air inlet is shown at D, the gauze at C, and the mantle at E.

In other types of inverted burners there is no fine adjustment for the gas, which enters the burner through a series of fine holes, as in the upright burner.

To obtain the most suitable flame for an inverted burner, adjust the gas and air supplies, after removing the mantle, until the length of the inner cone of the flame is approximately twice the diameter of the nozzle of the burner, and the gas burns without noise.

As in the case of the upright burner, the flame obtained before the mantle is in position should be perfectly non-

luminous, or a deposit of soot will be obtained on the mantle.

When replacing a globe of an inverted burner, the screws supporting the globe must be left slightly loose to allow for expansion.

A comparison of the amounts of gas consumed by a batswing and an incandescent burner should be made by means of the experimental meter, and a comparison made of the intensity of the illumination obtained with the two flames, by means of a simple photometer (see textbooks on Physics).

The Illuminating Power of Coal Gas.

For the official method of testing coal gas for illuminating power see "Notification of the Gas Referees," 1918, p. 5.

In connection with the use of coal gas for purposes of illumination, the terms "candle power" of a flame and of a gas require some explanation.

The unit of illumination (1 candle power) is that obtained from a standard sperm candle, of which there are six in one pound, burning at the rate of 120 grains in one hour. For practical purposes, however, the Harcourt pentane lamp, which has a candle power of ten, is usually employed.

By a flame of x candle power it is understood that the illuminating power is equal to that of x standard candles. By a coal gas of y candle power it is understood that the gas is burnt at a specified rate (5 cub. ft. per hour, measured at 60° F. and 30 ins. of mercury and saturated with water vapour) in a standard Argand lamp, and that the flame produced has an illuminating power equal to that of y standard candles.

The illuminating power of coal gas, as supplied before the war in various parts of this country, varied from 13 to 20 candles.

With a flat flame burner (fish-tail or batswing) the illumination produced with coal gas, as at present supplied, is probably less than 2 candles per cubic foot of gas burnt per hour, whereas with an upright incandescent burner an efficiency as high as 15 to 25 candles per cubic foot of gas burnt may be obtained. Thus, on this basis with an average coal gas, an ordinary upright incandescent burner, consuming 6 cub. ft. of gas per hour, would give a flame of from $6 \times 15 = 90$ to $6 \times 25 = 150$ candle power. With an inverted incandescent burner a still higher efficiency is obtained.

Until quite recently it was necessary that coal gas should conform to a legal standard as regards illuminating power; in view, however, of the general adoption of incandescent lighting, and the necessity for the removal of aromatic hydrocarbons from the coal gas for the manufacture of explosives, this restriction has been largely removed. It is probable, however, that a standard of calorific power (see p. 234) will be substituted for it at a later date. In this connection it should be noted that at the present time, if the gross calorific power of the gas is not less than 450 B.Th.U. (113 Cal.) per cub. ft., the test for illuminating power may be omitted.

The Pressure at which Coal Gas is Supplied.

In connection with the use of coal gas for purposes of incandescent lighting and for heating, the pressure (i.e. the excess of pressure over that of the atmosphere) at which the gas is supplied is a matter of considerable importance. The amount of primary air drawn into the burner is dependent on the velocity of the coal gas which enters, and this velocity obviously depends on the pressure of the gas. This pressure may easily be measured by means of a U tube containing water as shown in the diagram, Fig. 22.

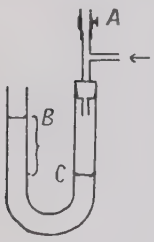


FIG. 22.

The U tube carries a T tube, one limb of which is attached to the gas supply and the other fitted with a short length of rubber tubing carrying a screw-clip.

Turn on the gas and close the screw-clip on the rubber tube A. The difference in level between B and C gives the pressure of the gas in inches of water. This pressure usually varies from 2 to 4 ins.

In connection with the use of coal gas for incandescent burners and gas fires, it is very essential that the gas pressure should remain constant (see p. 224).

For the official method of testing the pressure at which gas is supplied see "Notification of the Gas Referees," 1918, p. 11.

High Pressure Gas.—Within the last few years in certain towns, gas has been supplied at pressures up to 50 ins. of water for purposes of street lighting, etc. Owing to this high pressure, the gas enters the incandescent burner at a very

high velocity, and the amount of primary air drawn into the burner is sufficient for the complete combustion of the gas. A flame at a very high temperature is obtained and consequently the efficiency of the mantle is considerably increased. Owing to the high velocity of the gaseous mixture through the burner, striking back does not take place.

With high pressure gas the illumination produced is often as high as 50 to 70 candles per cubic foot of gas burnt per hour.

Incandescent Mantles.

In the manufacture of incandescent mantles, a woven ramie fabric is first soaked in a solution of thorium nitrate containing 1 per cent. of cerium nitrate. After drying, the organic matter is burnt off and a skeleton of oxides, produced by the decomposition of the nitrates, is obtained. This is treated with collodion (see p. 110) for protection, and the collodion burnt off after the mantle is placed in position on the burner.

The explanation usually given of the great efficiency of an incandescent mantle, consisting of a mixture of 99 per cent. thorium oxide and 1 per cent. cerium oxide, is that the particles of ceria, being embedded in a badly conducting mass of thoria, become very strongly heated. These particles of ceria also appear to have a catalytic action on the combustion of the coal gas, which tends to raise their temperature. If, however, a larger amount of ceria is present, the catalytic action of the substance is more than counter-balanced by its loss of heat by radiation, ceria being a substance which radiates heat freely.

For details regarding the manufacture of incandescent mantles see "Chemical Discovery and Invention in the Twentieth Century," by Tilden (Routledge), and article on "Gas Mantles," Thorpe's "Dictionary of Applied Chemistry" (Longmans).

GAS FIRES.

In connection with the use of coal gas for gas fires, it will be noticed that at the present time the most efficient gas fires consist of a series of Bunsen jets, which are surrounded by upright, perforated fireclay tubes, or so-called "radiants". The advantage of this arrangement is that complete combustion of the gas is ensured, which is not the case in a gas fire where

the flames are distorted by balls of fuel, as in some of the earlier forms of these fires (see p. 231).

In a good modern gas fire approximately 50 per cent. of the heat generated by the combustion of the gas is obtained as radiant heat, 15 to 25 per cent. as "convected" heat and 25 to 35 per cent. as flue heat,* whereas with the older types of gas fires the figures for heat radiated and convected were reversed. For effect of this on the relative humidity, etc., of the air of a room see page 182.

The corresponding figures for an open coal fire, using a good modern grate, vary considerably; they are, according to A. H. Barker, approximately as follows:—

Radiation	25 per cent.
Convection	5 „ „
Conduction	15 „ „
Chimney loss . . .	55 „ „

For a hot water "radiator" the figures are approximately:—

Convection	88 per cent.
Radiation	12 „ „

With the earlier types of gas fires it was usual to attempt to counteract the diminution of the relative humidity of the air, due to the heating of the air by convection, by placing a bowl of water near the fire, but with the modern gas fire, owing to the relatively small amount of the heat appearing as convected heat, the provision of this water is unnecessary.

The thorough admixture of gas and primary air in appropriate proportions, in order to obtain the maximum flame temperature and noiseless combustion, is of great importance in connection with the use of coal gas for gas fires, and a large amount of work has been done with reference to the design of burners for such purposes. It should be noted that if the burner is set, as regards admission of primary air, for a coal gas of a certain composition and density, and at a given pressure, any marked deviation from this composition and pressure will diminish the efficiency of the gas fire.

In examining a gas fire, note the arrangement for the fine control of the gas supply, placed between the main tap of the gas fire and the burner, and also the method adopted for increasing or diminishing the amount of primary air admitted.

* For method by which these quantities of heat are determined for a gas fire see Report of Gas Heating Research Committee (*Proc. Inst. Gas Eng.*, 1909-1911).

A considerable amount of work has also been done with reference to the size of the canopy above the gas fire, and the determination of the distance from the bottom of the canopy to the top of the radiants, which gives the best results. If the canopy is too near the radiants, too much air is drawn over them and they are thereby cooled. Since the radiation of heat from a source varies as the fourth power of the temperature of that source, it is obviously important to keep the temperature of the radiants as high as possible.

If all the products of combustion of a gas fire are removed, the amount of carbon dioxide in the air immediately adjacent to the gas fire canopy should not be greater than at a point four or five feet away. The determination of the carbon dioxide in air taken at these points,* will therefore give an indication as to whether or not the products of combustion are being efficiently removed.

It should be noted that in addition to the air drawn into the flue through the canopy of a gas fire, a certain amount of air is drawn past the sides of the fire owing to the up draught caused by the hot products of combustion. If the outlet pipe attached to the canopy is carried a short distance up the chimney, it acts as an injector and the ventilating action of the gas fire is thereby enhanced.

The Radiation of Heat from Flames.

Comparison of the Amounts of Heat Radiated from (a) a Bunsen Flame, (b) a Bunsen Flame surrounded by a Gas Fire "Radiant".

The fact that the amount of heat radiated from a Bunsen flame, which under ordinary conditions is about 12 per cent. of the total heat generated, is very greatly increased when the flame is surrounded by a fireclay "radiant" may be illustrated as follows. [It is perhaps unnecessary to point out that the *total* amount of heat *generated* in both cases is the same, if the same quantity of gas is consumed, but it is the proportion of heat *radiated* to heat *convected* which is increased by the fireclay radiant.]

Arrange two Bunsen burners to give similar flames at a distance of about 16 inches apart. The internal diameter of the Bunsen tubes should be about 1·3 cms. If such burners

* A sample of air for analysis by Pettenkofer's method in such a case may be taken by employing a small hand bellows or ball syringe (see p. 184).

are not available, short lengths of brass tube of this diameter may be placed over ordinary Bunsen burners.

Suspend a gas fire radiant over one of the flames by means of a piece of thick copper wire. When this radiant has reached its maximum brightness, place a board carrying a thermometer with blackened bulb on each side of the board, exactly midway between the two burners. The bulbs of the thermometers should be at the same height and approximately opposite the centre of the radiant.

Note the time required for the thermometers on each side of the board to register a rise of 5° C. and the temperature indicated by each thermometer after five minutes. It will be found that the thermometer exposed to the "radiant," at the end of a given time, registers a temperature which is considerably higher than that shown by the other.

Instead of thermometers, tubes containing a layer of a mixture of diphenylamine, $(C_6H_5)_2NH$ (4 parts), and para-nitrobenzaldehyde, $C_6H_4(NO_2)CHO$ (1 part), may be employed. This mixture when heated to 100° F. assumes a deep red colour which disappears on cooling. If such tubes are employed note the time for the red colour to appear in both cases.

The tubes containing this mixture are filled as follows:—

Some of the solid mixture of diphenylamine and the nitro compound is placed in a test-tube and melted. Another test-tube of slightly smaller diameter is then placed in this tube, so that the liquid forms a thin layer between the tubes. On cooling, the red liquid forms a colourless solid.

The amounts of heat radiated from the two sources may also, of course, be compared by means of a thermopile connected to a galvanometer.

GEYSERS.

Geysers are made either on the "open" or "closed" (sealed) principle. In the former type the hot gases from the burner come into actual contact with the water, whereas in the closed type the heat passes through a copper partition to the water. The advantage of the latter type is that, if the apparatus is suitably constructed, the geyser can be connected directly to the water supply, as in the so-called "circulators," and hot water obtained in any part of the house. In the open type of

apparatus the water must be delivered at a lower level than that at which it enters the geyser.

A vertical section of a Richmond "Cam" Geyser is shown in Fig. 23. The arrows indicate the direction of flow of the water.

In modern geysers the gas is usually burnt by means of a

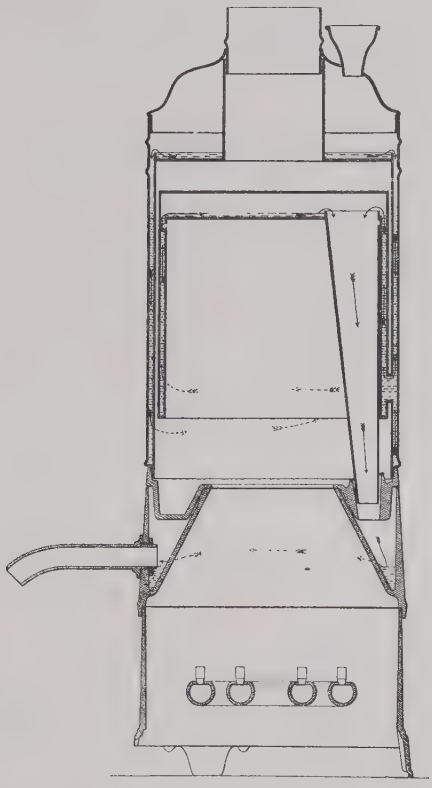


FIG. 23.—Section of Geyser.

series of flat flame burners. Many cases of carbon monoxide poisoning were due to the employment of Bunsen burners in the earlier and badly ventilated types of apparatus. As will be shown later, if the inner cone of a Bunsen flame is distorted, carbon monoxide is found among the products of combustion of the gas (see p. 231). Another advantage of the use of luminous flames is in connection with the automatic arrangement, which is attached to many modern geysers,

whereby the gas supply is cut down when the water in the apparatus has reached a certain temperature. With a Bunsen burner fitted with such an arrangement there is always a tendency to strike back.

Determination of the Efficiency of a Geyser.

The value of a geyser will obviously depend on the extent to which the heat generated by the combustion of the gas is absorbed by the water.

The percentage of the heat generated, which is thus absorbed, is termed the *efficiency* of the apparatus.

This is determined experimentally as follows :—

Note.—Before lighting the burner of the geyser it is important that water should be running through the apparatus, and the gas must be turned off before the water when the experiment is completed.

Allow the gas consumed by the burner to pass through an experimental meter (see p. 244) before it is burnt in the apparatus, and in this way determine the amount of gas (in cubic feet) consumed per hour. This may be found from one minute observations on the inner large dial, Fig. 31 (taking the average of several readings), or by noting the change of reading of the dials during ten minutes whilst the gas is burning.*

Note the temperature at which the water enters and leaves the apparatus.

Collect the water delivered by the apparatus in one minute in a suitable vessel, and find its volume by means of a measuring cylinder. Take the average of three determinations. Assuming the gas to have a certain calorific power (see p. 242), all the data are now available for calculation of the efficiency of the apparatus.

Example.

From a very small geyser the water was delivered at the rate of 1 litre (= 1 kg.) per minute, or 60 kg. per hour.

* In the case of a geyser which is already fixed in position, the amount of gas consumed per hour may be determined from readings taken by means of the small upper dial of the ordinary gas meter. With a small "five light" meter one revolution on this dial represents 2 cub. ft. (see p. 243). From the time taken for the consumption of this amount of gas, the hourly rate of consumption may be calculated. It will be obvious that during this experiment the burner under the geyser must be the only one which is in use.

Initial temperature of water, 21° C.
Final „ „ „ 56° C.

Rise of „ „ „ 35° C.

Consumption of gas, 662 litres per hour

$= \frac{662}{28{\cdot}3}$ cub. ft. = 22 cub. ft. „ „ (1 cub. ft. = 28·3 l.).

The calorific power of the gas = 120 Cal.* per cub. ft. *gross* (see p. 237), as supplied to burner.

Heat generated per hour by combustion of gas = 22 × 120 = 2640 Cal.

Heat absorbed by water per hour, i.e. mass of water in kg. × rise of temperature = 60 × 35 = 2100 Cal.

∴ Out of 2640 Cal., 2100 Cal. are utilised in heating the water.

∴ Out of 100 Cal., $\frac{2100 \times 100}{2640} = 79{\cdot}5$ are utilised.

Efficiency of apparatus = 79·5 per cent.

The efficiency of modern geysers usually varies from 80 to 90 per cent.

It should be noted that the efficiency of a geyser will vary slightly according to the temperature at which the water is drawn off from the apparatus. The higher this temperature, the lower is the efficiency.

An apparatus constructed on the same principle as the geyser having 100 per cent. efficiency (or more probably about 99·5 per cent.) is made use of in determining the calorific power of a gaseous fuel (see p. 234).

Further Determinations of Efficiencies.

As another example on the determination of efficiencies, find by experiment the percentage of the heat generated at a gas ring which is utilised in heating a given mass of water in various vessels.

Example.

A pint of water (1¼ lb. or 567 gms.) was heated in a heavy enamelled iron saucepan, fitted with a lid, from 15° C. to 100° C. in eight minutes.

* 1 Cal. (kilogram-calorie = 1000 calories) is the amount of heat to raise the temperature of 1 kg. of water 1° C.

The rate at which the gas was burnt was 225 litres (7·95 cub. ft.) per hour.*

∴ Amount of gas burnt in eight minutes

$$= \frac{7{\cdot}95 \times 8}{60} = 1{\cdot}06 \text{ cub. ft.}$$

Calorific power of gas = 120 Cal. per cub. ft. (*gross*).

Heat generated by 1·06 cub. ft. = 120 × 1·06 = 127·2 Cal.

Heat required to raise the temperature of 567 gms. (1 pint) of water from 15° C. to 100° C. = 567 × 85 = 48195 calories = 48·2 Cal.

Thus of 127·2 Cal. generated, amount utilised in heating the water alone † = 48·2 Cal.

∴ Of 100 cal. generated, amount utilised in heating the water alone $= \frac{48{\cdot}2}{127{\cdot}2} \times 100 = 38$, or efficiency = 38 per cent.

The experiment should be repeated, using the saucepan without lid, and using a thin aluminium saucepan and other vessels.

In view of the fact that a large amount of gas is often wasted by having too large a flame at a gas ring, with the consequent escape of partly burned gas, which not only has an objectionable smell, but also contains carbon monoxide, some of these experiments should be repeated, using a very large flame, and the results compared with those previously obtained. By plotting efficiencies against gas consumptions for a given gas ring, the curve obtained will show under what conditions the maximum efficiency is obtained.

It will be seen from the results of these experiments that only a small portion of the heat generated at the burner is used in actually heating the water.

With an electrically heated kettle the efficiency varies from about 60 to 85 per cent., according to whether the "elements" are in a hot plate, or in the body of the kettle, but in comparing gas and electric heating the relative cost of gas and electricity must, of course, also be taken into account (see p. 263).

With a coal fire it is very difficult to estimate the efficiency; for example, in boiling a kettle, if a fire were lighted especially for this purpose only about one or two per cent. of the heat

* Instead of using a special meter for this purpose, the experiment may be performed with the ordinary household appliances, taking the reading of the gas consumption from the small upper dial of the gas meter as explained on p. 243.

† i.e. neglecting the water equivalent of the containing vessel.

generated would probably be used in heating the water, whereas if the fire is already burning the efficiency of the process may be regarded as anything up to 100 per cent., since putting the kettle on the fire, in this case, does not increase the consumption of coal.

As a further example on efficiencies it is of interest to calculate the weight of coal required, theoretically, to heat the water contained in a bath of given dimensions.

If the bath (5 × 2 ft.) is filled with water to a depth of 1 ft., the volume of water required = 10 cub. ft. = 283 litres = 280 kg. (approximately).

If the initial temperature of the water is 10° C. (50° F.) and the temperature of the water in the bath 38° C. (100° F.), the rise of temperature is 28° C.

Amount of heat required for heating 280 kg. of water through 28° C. = 280 × 28 = 7840 Cal.

If the calorific power of the coal used is 8000 Cal. per kg. (see p. 257), rather less than 1 kg. (2·2 lb.) of coal is thus all that is required, theoretically, for heating the water. It is hardly necessary to point out that in actual practice a quantity of coal considerably in excess of this amount would be required. For further information *re* efficiencies, etc., see article in "Nature," 1915, p. 490, by A. H. Barker.

DETECTION AND DETERMINATION OF CARBON MONOXIDE IN THE PRODUCTS OF INCOMPLETE COMBUSTION OF COAL GAS.

As mentioned previously in connection with the use of coal gas for gas fires and geysers, carbon monoxide will be present among the products of combustion of coal gas, if the inner cone of a Bunsen flame is distorted by any cold, solid object. If the temperature of the object is below that of the flame (about 1500° C.), as is the case when a Bunsen flame is employed to heat a vessel containing water, the temperature of the gas immediately in contact with the object is reduced below the ignition point, and so unburnt gas escapes with the products of combustion.

Heat a round-bottomed flask containing cold water directly (i.e. without gauze) by means of a Bunsen burner, and place the flask at such a height above the burner that the inner cone of the flame is slightly distorted. Collect slowly a sample

(1 litre) of air from above the flask, by means of a large inverted funnel placed over the flask and attached to a set of aspirators (see p. 195).

The aspirator bottle to which the inverted funnel is attached is full of water at the commencement of the experiment, and is supported above the other. By opening the clip on the aspirator tube the air is drawn in.

This sample of air is then tested for the presence of carbon monoxide,* by making use of the fact that iodine pentoxide, I_2O_5, heated to 130° C. is decomposed by carbon monoxide as follows:—

$$I_2O_5 + 5CO \rightarrow 5CO_2 + I_2.$$

The reaction may be made use of not only for the qualitative detection of carbon monoxide, but also for its quantitative determination. The reaction is extremely delicate, and it is

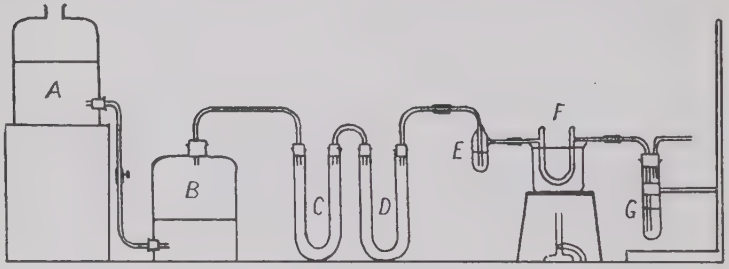


FIG. 24.

claimed that as little as 1 part of carbon monoxide in 40,000 parts of air may be detected by means of the test when only 1 litre of air is taken for the experiment.†

The apparatus employed for the test is shown in the diagram, Fig. 24. The gas under examination is contained in the aspirator B.

Before the gas passes through the U tube F containing glass beads and iodine pentoxide, it is freed from unsaturated hydrocarbons, sulphur dioxide and other reducing agents which would liberate iodine from heated iodine pentoxide. The

* If the sample is likely to contain an appreciable quantity of carbon monoxide, e.g. more than 1 per cent., the gas could be analysed by means of the Hempel apparatus, as in the case of coal gas (p. 207).

† The iodine pentoxide used in the experiment should be tested to make sure that it does not contain any free iodine and does not decompose spontaneously at the temperature to be employed in the test. This is carried out by passing a slow stream of air from the outside through the apparatus, before the aspirator containing the sample to be tested is attached.

removal of these substances is effected by passing the gas through a U tube C containing pumice moistened with sulphuric acid, and another U tube D containing solid potassium hydroxide. The caustic potash also removes carbon dioxide from the gas, so that the presence of carbon dioxide in the gas leaving the U tube F, containing iodine pentoxide, is an indication of the presence of carbon monoxide in the gas under examination (see equation, p. 232).

The small wash bottle E contains concentrated sulphuric acid.

The test tube G contains a small amount of a 2 per cent. solution of sodium hydroxide. Any iodine liberated from the iodine pentoxide is retained in this solution with formation of sodium hypoiodite and iodide.

The oil bath containing the iodine pentoxide U tube is heated to 130° C., and the gas is passed very slowly through the apparatus (at the rate of about 1 litre in an hour).

The level of the liquid in the aspirator bottle, B, at the commencement and end of the experiment is noted, and the volume of air which is tested (about 1 litre) is thus measured.

The temperature of the oil bath must not be allowed to rise appreciably above 130° C., as above 165° C. the iodine pentoxide will begin to decompose spontaneously, and any hydrogen in the gaseous mixture might reduce the iodine pentoxide.

Before commencing the experiment the apparatus is tested to make sure that it is gas-tight. This may be done by closing the exit tube from G, when, on opening the screw clip on the rubber tube between the aspirator bottles, no stream of gas should pass through G, or through the small wash bottle E containing concentrated sulphuric acid.

When a sufficient volume of gas has passed through the apparatus, the test tube G is disconnected. About 0·2 gm. of sodium nitrite is added to the sodium hydroxide solution and then dilute sulphuric acid until the liquid is just acid. 20 c.c. of chloroform are then added and the mixture shaken vigorously.

A pink coloration in the chloroform extract denotes the presence of iodine, which has been liberated by the action of the carbon monoxide on the iodine pentoxide.

The amount of iodine which has been liberated may be determined by transferring the chloroform extract to a stoppered bottle, after washing in a separating funnel with a small

quantity of a 1 per cent. solution of sodium bicarbonate to remove sulphuric acid, and titrating with N/100 sodium thiosulphate solution, using starch as indicator. After each addition of sodium thiosulphate the mixture must be thoroughly shaken.

From the volume of sodium thiosulphate solution required, the amount of iodine liberated is calculated in the ordinary way, see p. 137. From the equation on page 232, it will be seen that the liberation of 2 × 127 gms. of iodine corresponds to 5 × 22·4 litres of carbon monoxide at N.T.P. Knowing the volume of air tested, the percentage of carbon monoxide in the air is thus found.

The amount of iodine present may, however, be determined, approximately colorimetrically, by treating a measured volume of a standard solution of potassium iodide (0·1 gm. per litre) with sodium nitrite and dilute sulphuric acid, followed by extraction with 20 c.c. of chloroform.

The colour of the chloroform extract is compared with that obtained in the test. The amount of the standard solution of potassium iodide employed is varied, until the colour of the solution of the iodine in chloroform is the same as that in the test experiment. From the amount of potassium iodide required, the amount of iodine liberated by the carbon monoxide may be calculated.

DETERMINATION OF THE CALORIFIC POWER OF COAL GAS BY MEANS OF THE BOYS GAS CALORIMETER.

[A full description of the apparatus and method of using it is given in the "Notification of the Gas Referees for 1918," and in "The Calorific Power of Gas," by J. H. Coste (C. Griffin).]

The general arrangement of the apparatus is shown in the diagram, Fig. 25. The gas passes through a wet meter A and a governor (pressure regulator) B to the burner of the calorimeter C. The meter described on page 244 may be employed for this purpose (1 revolution on large dial = 2·5 litres), but in the official method of testing a meter is employed in which one revolution of the meter hand denotes the passage of $\frac{1}{10}$ cub. ft. (2·36 litres), the dial being divided into 100 divisions.

The use of the governor B is to ensure that the pressure of the gas, as supplied to the burner, remains constant, that is, the gas is burnt at a uniform rate.

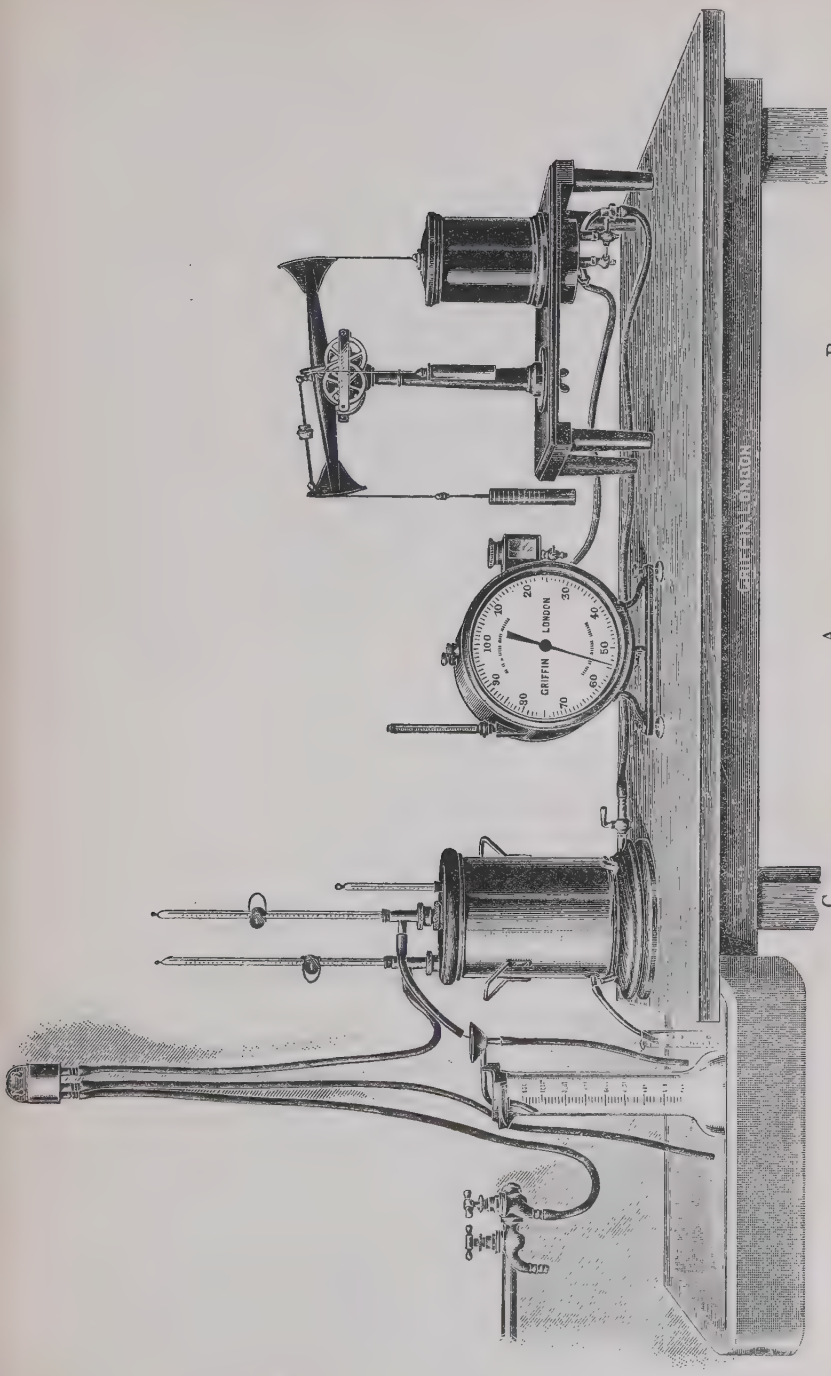


FIG. 25.

The Gas Governor.

The construction of this part of the apparatus and its mode of action is illustrated by the diagram, Fig. 26.

The inverted bell or gas holder E is suspended in water from one end of a beam, which rests on a knife edge at K. The gas enters the bell by the pipe shown at D. The upper end of this inlet pipe can be closed partially, or completely by means of a conical plug F attached to the bell. It will be seen that as the bell rises the inlet becomes closed, and is opened as the bell descends. The outlet pipe from the bell is shown at G. If the gas is unable to escape from this outlet pipe to the burner as fast as it enters through D, the bell E and plug F rise so that the gas supply to the bell is cut down. If on the other hand, the gas supply through D should diminish momentarily, the bell and conical plug F fall, and more gas is allowed to enter the bell. In this way the pressure of the gas leaving the outlet pipe is kept constant.

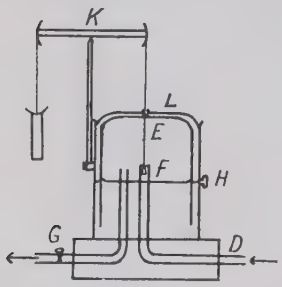


FIG. 26.

Before the apparatus is used, water should be poured round the bell (by removing the cover L, with the gas inlet closed and the outlet open) until it flows from the hole at H, which is then closed by means of a screw plug.

The Calorimeter.

The construction of the gas calorimeter C is shown in section in Fig. 27.

The main features of the instrument are as follows :—

The cold water from the constant level arrangement (see Fig. 28, p. 238) enters at O and passes through a coil of metal pipe, covered with coils of wire to facilitate the absorption of heat, round the outer part of the apparatus to the lower part. It then passes upwards, through a similar coil joined to the former, round the chimney of the calorimeter into a mixing box K, and then to the outlet P.

The inner and outer coils are separated by a partition Q containing cork dust for purposes of heat insulation.

The products of combustion first pass up the chimney E, and then downwards over the inner coil, through which the

water is passing, and finally in an upward direction over the outer coil, *thus leaving the calorimeter by the holes in the wooden cover at practically the same temperature as that of the incoming water.* The lowest turns of the coils of metal pipe through which the water is passing are immersed in water, which is poured in through one of the air outlet holes at the top of the apparatus until it flows from the pipe F. The water, produced

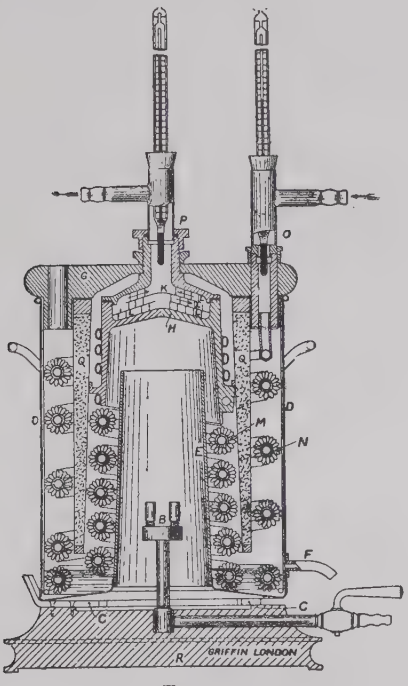


FIG. 27.

by the combustion of the hydrogen and hydrogen compounds in the gas, condenses and mixes with this water.

In this way the *gross*, or maximum, calorific power of the gas is obtained (see p. 241).

The temperature of the water at the inlet and outlet is taken by means of thermometers graduated in tenths of a degree centigrade. The temperature of the gases leaving the calorimeter is taken by means of an ordinary Fahrenheit thermometer.

The air required for combustion enters the apparatus through holes round the edge of the wooden base R. The metal base plate of the calorimeter is kept brightly polished

to prevent leakage of heat through the base of the apparatus.

It is important that the water should pass through the calorimeter in the direction indicated, otherwise the products of combustion will leave the apparatus hot and an incorrect result be obtained.

The latest form of the apparatus has a change-over funnel fixed to the wooden cover, by means of which the water leaving the apparatus may be allowed to run to waste, or be directed into a measuring cylinder.

The apparatus is very conveniently arranged so that the wooden cover to which the water coils, etc., are attached can be lifted off from the metal body containing the chimney. This part in its turn is simply lifted off the base vertically, and by examining the instrument in this way certain details of construction become at once apparent.

[*Note.—On no account must the calorimeter be re-assembled,* IF THE GAS IS BURNING, *unless a stream of water is flowing through the apparatus, and water has been poured in until it flows from F, Fig. 27.*]

The Constant Level Water Supply Apparatus.

The construction of this part of the apparatus is shown in the diagrams, Fig. 28.

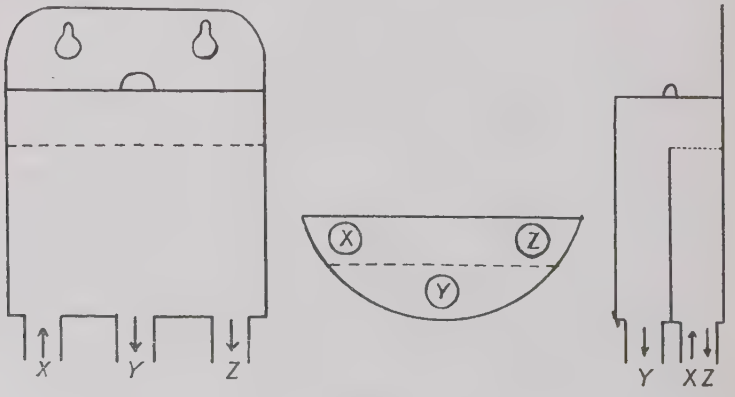


FIG. 28.

The inlet X is attached to a main water supply tap, and the rate of flow of water from this tap adjusted so that some water passes over the weir to waste through Y. The outlet pipe Z, attached to the inlet of the calorimeter, is on the same

side of the weir as the inlet pipe X. If water is always flowing over the weir, a constant head of water for the outflow to the calorimeter is maintained, which thus ensures a uniform rate of flow through the instrument.

The rate of flow of water through the calorimeter should be such that not less than 1600 c.c. pass through in four minutes, and not more than 2400 c.c. in five minutes. This rate may be adjusted by altering the height of the constant level apparatus above the sink, or by placing in the inlet rubber tube of the calorimeter a piece of brass tube, one end of which is closed by a diaphragm containing only a small hole. It should be noted that if the thermometers are placed too low in the inlet and outlet tubes, the flow of water is unduly restricted.

Method of Using the Apparatus.

After having removed the lid and body of the calorimeter, the gas jets may be lighted, and the gas supply regulated so that the large hand of the meter makes one revolution (2·5 litres) in from 65 to 75 seconds. [The official rate is $\frac{1}{12}$ cub. ft. (2·36 litres) in 60 to 75 seconds.] When the gas supply has been regulated to this rate, the body and lid of the calorimeter may be replaced, *provided a stream of water is flowing through the instrument, and water has been poured in through one of the air outlet holes until it flows from F, Fig. 27.*

The apparatus is now allowed to remain undisturbed for half an hour. At the end of this time it may be assumed that all the heat produced by the combustion of the gas is being absorbed by the water flowing through the apparatus.*

When the large hand of the meter is approaching the zero, take the temperature of the inlet water, and when the hand is exactly passing the zero, move the funnel, into which the water leaving the calorimeter is flowing, so that the water is delivered into the large graduated cylinder standing in the sink. Note the time exactly at which this is done. Allow the large hand of the meter to make *four* complete revolutions (10 litres of gas burnt), taking the temperature of the inlet water after every complete revolution, and the temperature of the outlet water after every *half* revolution.

When the meter hand passes the zero at the end of the fourth revolution, move the funnel so that the water leaving the calorimeter is directed into the sink. Note the time exactly

* See, however, corrections to be applied, p. 241.

and so calculate the time taken for the test. (See *net* calorific power, p. 241.)

Take the average of the temperature readings of both the inlet and outlet water, and note the volume of water collected in the large cylinder. [Note the readings of the thermometers showing the temperature of the effluent gases from the calorimeter and of the gas in the meter. Take the reading of the height of the barometer in inches (to the second decimal place), and the reading of the wet- and dry-bulb thermometers of the ventilated hygrometer (see p. 241, and "Notification of the Gas Referees," 1918, p. 27.]*

All the data are now available for the calculation of the gross calorific power of 1 cub. ft. of the gas as supplied to the burners, or by applying various corrections, the gross calorific power of 1 cub. ft. of the gas, measured at 60° F., under a pressure of 30 inches of mercury and saturated with water vapour.

The difference between the average temperature of the inlet and outlet water multiplied by the number of cubic centimetres of water collected during the test will give the number of calories produced by the combustion of 10 litres of the gas.† This value divided by 1000 gives kilogram calories. From this calculate the heat evolved by 1 cub. ft. (28·3 litres) of the gas as supplied to the burner.

Example.

Average temperature of outlet water, 34·85° C.

" " " inlet " 15·15° C.

Rise of temperature, 19·7° C.

Volume of water collected, 2105 c.c.

Heat generated by $4 \times 2{\cdot}5$ (= 10 litres) of gas = $2105 \times 19{\cdot}7$ = 414685 calories = 414·7 Cal.

∴ Heat generated by 1 cub. ft. (28·3 litres)

$$= 414{\cdot}7 \times \frac{28{\cdot}3}{10} = 117{\cdot}4 \text{ Cal.}$$

$$= 117{\cdot}4 \times 3{\cdot}968 = 468{\cdot}2 \text{ B.Th.U.}‡$$

* These readings are taken if the corrections noted on p. 241 are to be applied.

† Although it would be more accurate to weigh the water for this calculation, it is usual to measure its volume.

‡ 1 Cal. (kilogram-calorie) = 3·968 British thermal units (B.Th.U.). This is arrived at as follows:—

1 Cal. would raise the temperature of 2·2046 lb. (1 kg.) of water 1° C. or 1·8° F.

∴ 1 Cal. would raise the temperature of $2{\cdot}2046 \times 1{\cdot}8 = 3{\cdot}968$ lb. of water 1° F.

1 B.Th.U. raises the temperature of 1 lb. of water 1° F.

∴ 1 Cal. = 3·968 B.Th.U.

Thus the calorific power of 1 cub. ft. of the gas as supplied to the burners = 117·4 Cal. or 465·4 B.Th.U. (gross).

After use, the gas is turned off *before* the water, and the part of the calorimeter attached to the lid lifted out of the body of the apparatus containing the chimney, and supported in a jar containing water made alkaline with sodium carbonate. In this way any sulphuric acid produced in the combustion of the gas, and which adheres to the coils, is neutralised.

In the official method of testing the calorific power of gas certain corrections are made, so that the result is expressed as the gross calorific power of 1 cub. ft. of gas at 60° F., under a pressure of 30 inches of mercury and saturated with water vapour.

From the readings of the meter thermometer and the barometer, and by reference to a table "Notification of the Gas Referees," 1918, p. 12, a factor is obtained by which the gas volume must be multiplied in order to reduce it to these standard conditions.

Further, the relative humidity of the air entering the apparatus is taken into consideration. If this incoming air is comparatively dry, and is saturated with moisture when it leaves the apparatus, a certain amount of heat will be absorbed in evaporating the water necessary for this saturation. Data for this correction are obtained from readings of wet and dry bulb thermometers contained in a special form of ventilating hygrometer, and from the temperature of the effluent gases from the calorimeter. The method of calculating the amount of this correction is dealt with in "Notification of the Gas Referees," 1918, p. 10.

The Net Calorific Power of Gas.—It has been pointed out, p. 237, that in determining the calorific power of gas, the water produced by the combustion of the hydrogen and hydrogen compounds in the gas is allowed to condense, and is also cooled down below 100° C. The heat which is measured thus includes the latent heat of the steam condensed, and also that heat evolved by cooling this condensed water.

It is hardly necessary to point out that in actual practice this condensation, as a rule, does not take place, nor are the other products of combustion similarly cooled, so that even if allowance is made for the condensation of the water, in obtaining what is called the net calorific value, the correction is only a partial one and has not much significance.

In order to obtain the *net* calorific power of the gas, the amount of water condensed during the time the test is in progress must be determined. The water flowing from the pipe F., Fig. 27, in twenty minutes is collected in a measuring cylinder, and so the water condensing in the time taken for the test is calculated.

One gm. of steam at 100° C. in condensing to water gives out 536 calories = 0·536 Cal., and 1 gm. of water at 100° C. cooled to 16° C. gives out 0·001 × 84 = 0·084 Cal., so that if 1 gm. of steam at 100° C. is condensed and cooled to water at 16° C., the amount of heat evolved is 0·536 + 0·084 = 0·620 Cal. In this way the correction to be applied for the condensation and cooling of the water produced when 1 cub. ft. of gas is burnt may be calculated. This amount of heat deducted from the *gross* calorific power gives what is known as the *net* calorific power of the gas.

The *gross* calorific power of coal gas at the present time varies from about 113 Cal. (450 B.Th.U.) to about 125 Cal. (500 B.Th.U.) per cubic foot. Prior to the war this value was sometimes as high as 138 Cal. (550 B.Th.U.) to 150 Cal. (600 B.Th.U.) per cubic foot.

GAS METERS.

THE HOUSEHOLD METER.

A diagram showing the dials, etc., of a small type of dry gas meter is shown in Fig. 29.

In a *dry* gas meter the gas passes through a leather bellows arrangement, the movements of which set in motion a series of gear wheels. A pointer is attached to some of these wheels, and from the number of revolutions of each, the amount of gas passing through the meter is measured. Thus if the pointer of the right-hand dial makes one complete revolution, this is indicated by an increase of one unit of the reading of the centre dial, and so on.

In a wet meter the gas passes through a series of small gas holders attached to a central axle. As each gas holder becomes filled with gas it rises and the gas is discharged into another part of the meter. In this way a circular motion is imparted to a series of wheels as in the dry meter. In both cases the motion is due to the excess of pressure on the inlet side of the meter over that on the outlet side, when gas is passing through the meter.

It should be noted in taking the readings from the dials of a gas meter, that the motion of the pointer round some of the dials is in a clockwise direction, and in others contra-clockwise. The figures recorded in taking the meter reading are those which were last passed by the respective pointers. Thus the reading indicated on the dials represented in Fig. 29 is 29,800; each division on the right-hand dial representing 100 cub. ft., on the central dial 1000 cub. ft., and on the left-hand dial 10,000 cub. ft. In this case, therefore, the reading is taken to the nearest 100 cub. ft. As indicated below the dials, complete revolutions represent 1000, 10,000 and 100,000 cub. ft. respectively.

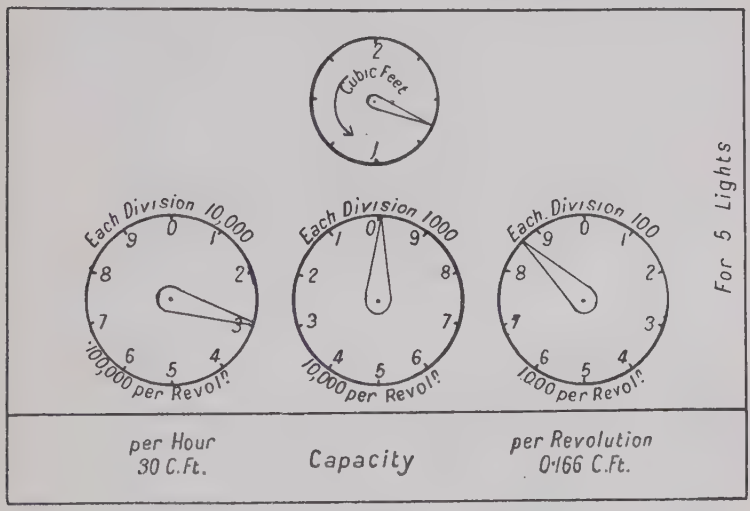


Fig. 29.

The upper small dial is thus not made use of in taking an ordinary reading of a gas meter, but is of use in detecting leakages and for experimental purposes. One revolution of the pointer over the dial shown represents the passage of exactly 2 cub. ft. of gas through the meter. A fraction of a revolution on this dial may not correspond exactly to the passage of that fraction of a cubic foot indicated, so that in making use of this dial in experiments it is better to take the time of one complete revolution (i.e. passage of 2 cub. ft.) and then to calculate the amount of gas used in the time occupied by any experiment (see notes, pp. 228 and 230).

The data given below the dials refer to the capacity of the

meter. For the meter indicated in Fig. 29, 30 cub. ft. per hour represents the maximum rate at which gas can pass through the meter, and 0·166 cub. ft. per revolution refers to the capacity of the bellows. The term "five light" meter is also employed to denote its capacity. Thus a meter with a capacity 30 cub. ft. per hour could be used on a supply for five jets, each of which required 6 cub. ft. per hour, or for a less number of jets with a greater hourly consumption, or a larger number of jets with a less hourly consumption.

In the case of a slot meter each time a coin is placed in the meter it becomes possible for a certain amount of gas to pass *through* the apparatus. The amount registered on the horizontal scale does not, of course, represent the quantity of gas which is contained in the meter, but the amount which can pass through it before the gas inlet valve is closed automatically.

THE EXPERIMENTAL METER.

In using the experimental *wet* meter, Fig. 30, make sure that the meter is vertical, as shown by the plumb-line. If it is not vertical, alter one or more of the foot screws in the stand on which the meter is fixed. Pour water into the meter, if necessary, through the thermometer attachment until it reaches the line on the circular glass plate. The water in the meter must be allowed to become saturated with gas before any readings of gas passing through the meter are taken.

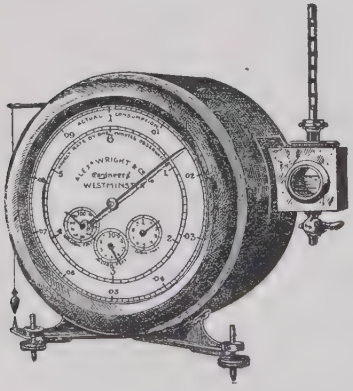


Fig. 30.

The quantity of gas passing through the meter in any experiment may be read off by means of the dials. The large inner dial is for calculating the hourly rate of passage of the gas through the meter, by observing the change of reading in one minute. Thus if the large hand has made one complete revolution and is passing the division 120 at the end of one minute, the amount of gas passing through the meter in one hour is 150 + 120 = 270 litres.* The maximum rate for the

* See Fig. 31, p. 245.

meter of which the dials are shown in Fig. 31 is 600 litres (= 21·2 cub. ft.) per hour. One revolution of the large hand

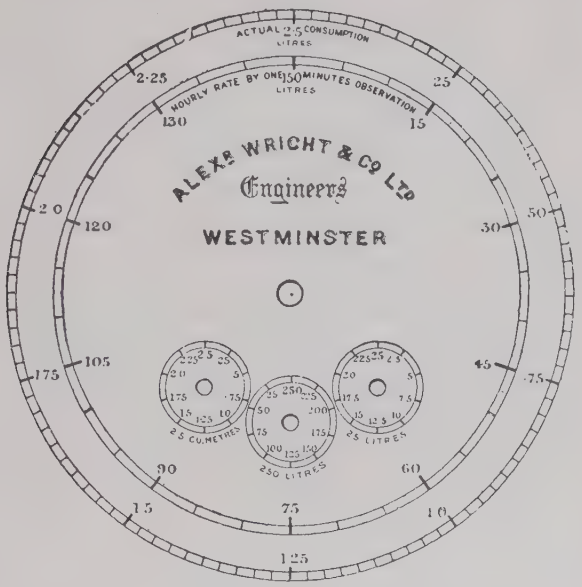


FIG. 31.

round the outer large dial represents the passage of 2·5 litres. The figures below the small dials denote the volume passing in complete revolutions.

CAUSES OF THE FAILURE OF THE GAS SUPPLY IN A HOUSE.

With a wet meter one of the principal causes of the failure of the supply is insufficient water in the meter. To remedy this defect, after turning off the tap on the inlet pipe of the meter and removing the screw plugs from the top and bottom of the meter, water is poured into the meter until it flows from the outlet near the bottom. The screw plugs are then replaced.

In winter the water in a wet meter may become frozen. Failure of the supply due to this cause may be overcome by applying cloths soaked in hot water to the lower part of the meter. It is of course better to protect the meter from the

cold before frost sets in. The addition of glycerine to the water in the meter is sometimes advocated to prevent freezing, but in view of the large amount of water contained in the meter, a considerable quantity of glycerine would be necessary to produce any appreciable lowering of the freezing-point of the water.

In some cases, both with wet and dry meters, owing to the accumulation of condensed water in the pipe, the passage of the gas becomes intermittent and may fail altogether. As a rule, at the lowest point of the supply pipe there is a plug (so-called siphon) which can be removed, and the water which has accumulated allowed to drain off.

In other cases an accumulation of solid naphthalene takes place in the pipes. This is usually removed, by the gas company's servants, by means of a compression pump and the use of a solvent oil.

Chapter IX.

LIQUID AND SOLID FUELS.

LIQUID FUELS.

THE FLASH POINT OF OILS.

It is obvious that owing to differences in volatility, inflammable liquids differ very considerably in the extent to which they give off inflammable vapours at the ordinary temperature. This may be illustrated by the following simple experiments.

Obtain three small beakers A, B and C; place about 10 c.c. of light petroleum (petrol) in A, 10 c.c. of paraffin oil (kerosene) in B, and 10 c.c. of medicinal petroleum or lubricating oil in C.

Remove the bottles containing the oils to a safe distance, and hold a lighted taper over the mouth of each beaker in turn. Note that the vapour in A only is ignited. Cover the mouth of this beaker with a piece of cardboard or a glass plate, in order to cut off the supply of air and so extinguish the flame of the burning vapour of the oil.

Lower the lighted taper into the beakers B and C alternately and note that the vapour of the paraffin oil is more readily ignited than that of the heavier oil in C, but that both these oils give off inflammable vapour much less readily than the oil in A.

It is, in fact, possible to extinguish a lighted taper by suddenly immersing it in paraffin oil. If, however, the temperature of the oils in B and C be raised, the vapours will be ignited when a lighted taper is placed over the mouth of the beaker.

The so-called *flash point* of an oil is the lowest temperature at which sufficient vapour is given off to ignite momentarily on the introduction of a spark or flame.

From the simple experiments described above, it is obvious that the flash point of petrol is below the ordinary temperature.

In the determination of what is known as the *closed test*

flash point, the oil is examined in an Abel flash point apparatus. Its temperature is raised slowly and the vapour given off from the oil is allowed to accumulate. A small flame is introduced periodically into the mixture of air and vapour above the liquid, and the temperature at which sufficient vapour has been given off to ignite, when the flame is introduced, is taken as the closed test flash point.

On account of the danger of using an oil with a low flash point for purposes of illumination in an ordinary paraffin lamp, and in other ways, the minimum closed test flash point for illuminating oils is fixed by law in this country at 73° F.

Determination of the Approximate Flash Point of an Oil.

Fill a large porcelain or metal crucible half full of the oil to be tested (paraffin oil or a heavy petroleum oil). Cover the mouth of the crucible with two pieces of asbestos, each of which has a slit cut half way across it just wide enough to fit round the stem of a thermometer.

Place the crucible on a sand bath and support a thermometer in the crucible so that the bulb is immersed in the oil. Turn the upper piece of asbestos round through two right angles, so that the mouth of the crucible is completely covered.

Draw this piece of asbestos forward and allow a small gas flame about 0·5 cm long (such a flame may be obtained by connecting a gas supply tube to a mouth blowpipe) to come into contact with the mixture of oil vapour and air in the crucible. No flash should be observed at the ordinary temperature.

Replace the upper asbestos and commence heating the sand bath, so that the temperature of the oil rises two degrees centigrade per minute. Test with the flame at the end of each minute. The flash point is taken as the temperature of the oil when the first of a series of flashes is obtained.

The use of paraffin oil and petrol for purposes of illumination and heating will be dealt with in the lectures.

ALCOHOL AS FUEL.

On account of the fact that alcohol burns with a non-luminous flame it is very suitable for purposes of heating in small scale operations. It is probable, however, that in addition to the use of so-called methylated spirit for these purposes,

large quantities of alcohol will be used before long in this country as a fuel for internal combustion engines.*

The question of the denaturing of alcohol, that is, the addition of substances to the alcohol so as to render it unfit for drinking purposes, is dealt with in the lectures.

Alcohol, unlike petrol and benzol (commercial benzene), is miscible in all proportions with water, so that the determination of the amount of alcohol in an aqueous solution of the substance is a matter of considerable importance.

If the solution contains only alcohol and water, the percentage of alcohol in the mixture is found by determining the specific gravity of the liquid, and by reference to tables, which show the amount of alcohol in solutions of the substance of different specific gravities. On account of the fact that when alcohol and water are mixed, the volume of the mixture is less than the sum of the volumes of the constituents, it is not possible to *calculate* the percentage of alcohol in an aqueous solution of the substance from the specific gravity of the mixture and the specific gravity of pure alcohol.

If the alcohol and water are mixed with other substances which are non-volatile, the liquid is distilled until about two-thirds has passed over. The distillate is then diluted with water to the original volume of the mixture distilled, and the specific gravity of the diluted distillate determined.

Determination of Alcohol in a Mixture.

For practice in the determination of alcohol by distillation, the percentage of this substance in one of the alcohol-soap mixtures, sold at the present time (as solidified methylated spirit) should be undertaken.

[One of these mixtures may be made by dissolving 3 gms. of stearic acid in 100 gms. of alcohol heated on the water bath to 65° C. The warm solution is then neutralised, after the addition of a few drops of a solution of phenolphthalein, by the addition of an aqueous solution of sodium hydroxide. On cooling the mass solidifies.]

Place 10 gms. of such a mixture in a distilling flask fitted to a water condenser. Add about 200 c.c. of distilled water and about 1 gm. of solid barium chloride, to precipitate the

* For further information on this subject and for an account of the preparation of alcohol on a small scale from potatoes see "Chemistry of Petroleum," by Tinkler and Challenger (Crosby Lockwood & Son). See also Report of Inter-Departmental Committee on "Power Alcohol," 1919 (H.M. Stationery Office).

soap, and so prevent frothing. Distil the mixture until about two-thirds has passed over.

Dilute the distillate to 200 c.c. by the addition of distilled water, and determine the specific gravity of the distillate at 60° F. (15·5° C.) by means of the specific gravity balance * (or specific gravity bottle). From the alcohol table "Quantitative Analysis," Clowes and Coleman, find the percentage by weight of alcohol in the distillate.

This value multiplied by two will give the weight of alcohol in 200 c.c. of the distillate, or in the 10 gms. of the original mixture.

SOLID FUELS.

PARTIAL ANALYSIS OF COAL.

It will be obvious that if results of any value are to be obtained in connection with coal analysis, great care must be exercised in taking a sample of the material for this purpose.

In order to obtain a sample representative of the whole bulk of the coal, a large quantity of the material must be broken up into small pieces, some of which are further subdivided until finally a portion is obtained which will pass through a 60 mesh sieve (60 meshes to the linear inch). This sample is then placed in a glass stoppered bottle.†

In examining coal the operations usually carried out involve determinations of moisture, volatile matter, ash and calorific power. It is, however, necessary in some cases to determine the percentages of carbon, hydrogen, nitrogen, sulphur, etc., in the coal.

Determination of Moisture and Ash in Coal.

Moisture.—Place 1 gm. of freshly powdered coal (60 mesh) in a weighed porcelain crucible (without lid), and heat in a constant temperature air oven for one hour at 105° C. Cool in a desiccator and re-weigh.

The loss in weight under these conditions is taken as the moisture contained in the coal, and from the result obtained the percentage of moisture may be calculated.

If the crucible be re-heated in the air oven, it will probably

* See note on p. 172.

[† For further information *re* sampling of fuels see "Fuel," by Brame (E. Arnold).]

be found impossible to obtain a constant weight, owing to the slow absorption of oxygen by the coal.

Ash.—Heat the crucible containing the dry coal gently over a Bunsen flame in a draught cupboard, and continue the heating over a full flame (or in a muffle furnace) until all the carbon has burnt away. Allow the crucible to cool in a desiccator and weigh when cold. From the weight of the ash obtained, calculate the percentage of ash in the original coal.

Determination of Volatile Matter.—This determination is of value in comparing one coal with another as regards coke yield, but only if the experiments are carried out under similar conditions. The reason for this is that in this determination the heating is continued only until the volatile matter of the coal has been removed, and what is known as "fixed carbon" is left unburnt. If the heating is prolonged the fixed carbon also burns.

Place 1 gm. of freshly powdered anthracite (60 mesh) in a porcelain, or preferably, platinum crucible, fitted with a lid, and 1 gm. of a freshly powdered bituminous coal in another similar crucible.

Support the crucibles on pipe-clay triangles, well above the flames of two similar Bunsen burners. Gradually lower the rings supporting the triangles until the crucibles are just above the inner cones of the flames.

Continue the heating for seven minutes in this position, making about ten minutes in all.

Allow the crucibles to cool in desiccators, and re-weigh to obtain the amount of coke produced.

Calculate the percentage of volatile matter in each case, making allowance for the moisture content of the samples.

It will be obvious that the results obtained in these determinations of volatile matter will depend on the extent of heating, and in order to compare the results obtained with those obtained by other workers it is necessary that the procedure should be the same. There is apparently at the present time no one standard method for this determination.

The percentage of moisture *plus* volatile matter in the anthracite will probably be less than 7 per cent., whereas with the bituminous coal the total loss in weight (moisture + volatile matter) may be as high as 40 per cent.

The anthracite will also probably contain less ash than the bituminous coal. In the latter case the ash will probably be

between 1 and 5 per cent., but as much as 10 per cent. may be found.

In carrying out a complete analysis of coal, the carbon and hydrogen may be determined by the ordinary process of combustion, and the nitrogen by the Kjeldahl process.

Sulphur is determined by heating the coal with a mixture of sodium carbonate and lime, whereby the whole of the sulphur is converted into soluble sulphates, the amount of which can be determined in the ordinary way.

THE CALORIFIC POWER OF COAL.

This value may be determined by means of either the William Thomson or the Rosenhain calorimeter. The most reliable results are, however, obtained by employing a so-called bomb calorimeter (see Vol. II.).

The William Thomson Calorimeter. — This apparatus (Fig. 32) consists of a glass combustion chamber, which fits on to a brass base by means of springs, and contains a platinum crucible in which the fuel to be burned is placed.

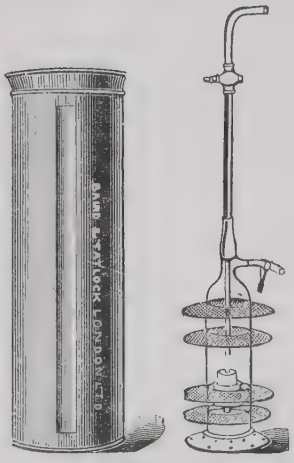


FIG. 32. — William Thomson Calorimeter.

Oxygen is passed in through the vertical tube, and the products of combustion and excess of oxygen escape through the holes in the brass support at the foot of the chamber.

The combustion chamber is surrounded by wire gauze baffle discs, which serve to break up the escaping gases into small bubbles, and thereby cause them to give up their heat entirely to the water.

This part of the apparatus is immersed in a measured amount of water at a known temperature, contained in a narrow, tall glass beaker, which is surrounded by a metal vessel fitted with a glass slip, through which the progress of the combustion may be watched.

Water is prevented from entering the combustion chamber owing to the slight pressure in this vessel due to the oxygen.

The combustion of the fuel is started by means of a small fuse, prepared by steeping a strand of cotton wick in a solution of potassium nitrate, and afterwards drying it.

The rise in temperature is observed by means of a thermometer graduated in tenths of a degree.

In the determination about 1 gm. of the fuel,* preferably in the form of a pellet,† is weighed accurately with the platinum crucible, which is then placed in its pipe-clay support.

Two thousand c.c. of water, taken from a vessel which has stood for some time in the room where the determination is to be made, are placed in the large beaker, and the temperature of the water accurately noted.

The thermometer should be suspended so that its bulb is about 5 cm. below the surface of the water.

An oxygen cylinder, fitted with a reducing valve, should be attached to a large wash bottle containing water, by means of rubber tubing, and the exit tube of this wash bottle attached to the brass inlet tube of the combustion chamber. The use of the wash bottle ensures that the oxygen supplied for combustion is saturated with water vapour. With dry oxygen the combustion is not so complete, and heat would be absorbed from the water in the calorimeter by the evaporation caused by bubbling dry oxygen through it.

In order to ensure that the oxygen is at the same temperature as the apparatus, it should be passed through a large coil of flexible metal tubing before passing into the wash bottle.

The oxygen inlet tube should be raised at first, so that its end is near the top of the chamber. A fuse of the prepared wick, about 2·5 cm. long, is then placed upright in the crucible and ignited. The combustion chamber is at once placed over the crucible, and the whole transferred to the beaker and immersed in the water, a gentle stream of oxygen being passed through the apparatus. The amount of oxygen supplied is regulated so that the combustion does not become too violent. When the combustion is nearly complete, the oxygen tube is lowered until its end is only slightly above the crucible.

When the combustion is at an end the oxygen supply is cut off, and the combustion chamber is raised so that the clip on the rubber tube attached to the side tube may be opened. On

* See p. 250 *re* sampling of coal.

† If the sample be in the form of a powder some of it may be thrown out of the crucible by the escape of volatile products.

again lowering the apparatus into the water, the gases from the combustion chamber will be driven out through this side tube, and water will come into contact with all parts of the apparatus which have been heated.

The contents of the beaker are then thoroughly mixed, by raising and lowering the combustion chamber, and the maximum temperature registered by the thermometer is noted. The time over which the combustion extends should also be noted. (See radiation correction below.)

In order to complete the calculation it is necessary to find the water equivalent of the calorimeter. This is determined in a separate experiment, by employing a given weight of a substance of known calorific value. Thus, if 1 gm. of a sample of standard coal, or of some other standard substance, is known to give 8500 calories on combustion, and the rise of temperature observed with 2000 gms. of water in the calorimeter is 3·8° C., then if x = the water equivalent of the calorimeter, the 8500 calories is taken up by $2000 + x$ gms. of water whereby the temperature is raised 3·8° C.

Amount of heat = mass of water heated × rise of tem-temperature.

$$\therefore\ 8500 = (2000 + x)3{\cdot}8$$

whence $3{\cdot}8x = 900$

$$\therefore\ x = 237.$$

That is, the water equivalent of the calorimeter is 237 gms.; or, 8500 calories will heat 2237 gms. of water 3·8° C.

2000 gms. of water were employed,

∴ water equivalent of calorimeter = 237 gms. of water.

In the determination described above, no notice is taken of the fact that heat will be lost from the calorimeter, during the combustion, by radiation, etc., whilst the temperature of the water is rising to its maximum value. This loss may be allowed for as follows, the correction being known as the *radiation correction*:—

After the maximum temperature is reached, the apparatus is allowed to cool for a period of time equal to *half* that taken for the combustion, a slow stream of oxygen being passed through the apparatus meanwhile, and the clip on the side tube being closed.*

* A period of time equal to *half* that required for the combustion is taken, on account of the fact that the temperature of the apparatus rises much more rapidly during heating than it falls when cooling. The greater the difference of temperature between the calorimeter and its surroundings, the greater is the

The fall of temperature, noted during this period, is added to the observed rise as the radiation correction.

Having found the water equivalent of the calorimeter and the radiation correction, we have all the data necessary for finding the calorific power of the given fuel.

Amount of heat evolved, in calories, by the combustion of a given weight of fuel

= (mass of water in calorimeter + water equivalent) × (rise of temperature + radiation correction).

From this the amount of heat evolved by the combustion of 1 gm. of the fuel in calories, or 1 kg. in kilogram-calories, or 1 lb. in British thermal units (B.Th.U.) may be calculated (see also p. 257).

The Rosenhain Calorimeter.—This calorimeter (Fig. 33) is a modified form of the William Thomson instrument. It differs from the latter in having an electric ignition, which is produced by passing a current through a short length of platinum wire. It is so arranged that this ignition device can be drawn out of contact with the fuel after combustion has started, otherwise it would be damaged in the course of the combustion and eventually destroyed.

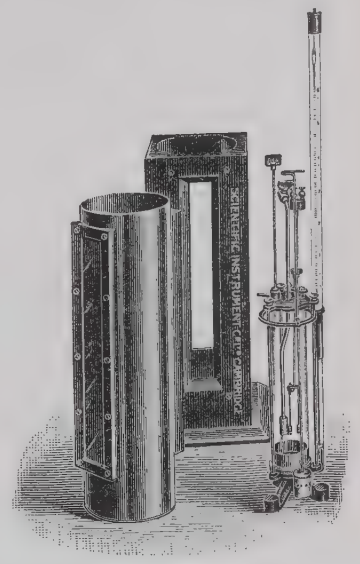


Fig. 33.—Rosenhain Calorimeter.

The combustion chamber consists of an ordinary incandescent lamp chimney closed at the ends by brass plates, the junctions being made gas-tight by means of rubber washers. The gases from the combustion chamber pass through a ball valve, which prevents the water from entering. When it is necessary to allow the water to enter, the ball can be raised by means of

loss of heat by radiation. It is assumed that as much heat is lost by radiation during the time of heating, as is lost in half that time when the apparatus is cooling.

the lever, and the outlet tap at the top of the chamber opened.

For the determination of the calorific power of a coal by means of this instrument, a weighed quantity of the substance (about 1 gm.) in the form of a pellet is placed on a silica tray in the combustion chamber, and the brass plates screwed together, care being taken not to screw too tightly.

The ignition wire is then placed in contact with the pellet. 2500 c.c. of water at the laboratory temperature are next introduced into the calorimeter vessel, and the latter placed in the wooden case. The combustion chamber is then lowered into the calorimeter, the thermometer placed in position, and a slow stream of oxygen, treated as in the previous determination, passed through the apparatus.

The temperature of the water, if constant, is noted as the *initial* temperature.

The pellet is now ignited by connecting up the battery (4 volts) for two seconds, after which the ignition wire is drawn up near the top of the combustion chamber. The time at which the combustion is started is noted.

The slow stream of oxygen is allowed to pass until combustion is nearly complete, when it is gradually increased in order to ensure total combustion. When the sample is completely burned, the oxygen supply is cut off, and water allowed to fill the combustion chamber by raising the ball of the valve, and opening the tap at the top of the combustion chamber. The water is then forced out by turning on the oxygen and closing the tap at the top of the chamber, the oxygen being allowed to pass through the apparatus in order to stir effectually the contents of the calorimeter. The thermometer is carefully watched, and the maximum reading is noted. This will be observed almost immediately after the water is expelled from the combustion chamber.

The time at which the maximum reading is observed is noted, and the whole apparatus is allowed to cool for half the time taken for the combustion. The fall in temperature is added to the observed rise of temperature of the water as the radiation correction (see p. 254).

The water equivalent of the apparatus is determined, as in the case of the William Thomson apparatus, by employing a sample of coal of known calorific value, the ignition wire being heated for the same length of time as in the previous case. The calculation of the calorific power of the coal is exactly

the same as described on page 255, and is illustrated by means of the following example *:—

Weight of pellet, 0·9945 gm.
„ „ water, 2000 gms.
Water equivalent of calorimeter, 239 gms.
Initial temperature, 12·62° C.
Final „ 16·06° C.
Rise of „ 3·44° C.
Radiation correction, 0·1° C.
Corrected rise of temperature, 3·54° C.
Heat evolved by combustion of the coal
$= (2000 + 239) \times 3{\cdot}54 = 7926$ calories $= 7{\cdot}926$ Cal.
Or 0·9945 gm. of coal give 7·926 Cal.

$$\therefore \text{ 1 gm. of coal gives } \frac{7{\cdot}926 \times 1}{0{\cdot}9945} = 7{\cdot}97 \text{ Cal.}$$

Or calorific power of the coal is 7·97 Cal. per gm., or 7970 Cal. per kg.

$$\text{Or } \frac{7970 \times 3{\cdot}968}{2{\cdot}205} = 14{,}340 \text{ B.Th.U. per lb.}$$

(1 Cal. = 3·968 B.Th.U.; 1 kg. = 2·205 lbs., see p. 240).

COAL ECONOMISERS.

Most of the preparations sold for this purpose consist largely of common salt with a little ferric oxide added. In some cases substances such as sodium carbonate, calcium carbonate or ammonium salts are also present.

The qualitative and quantitative analyses of such mixtures present no difficulties, and can be carried out by the ordinary methods.

It will be obvious that the addition of small quantities of these substances to coal cannot in any way increase the total amount of heat produced by the combustion of that coal. The use of these materials mixed with water might conceivably diminish the amount of combustible matter which escapes unburnt from the coal, and in this way diminish the amount of heat lost, but no definite evidence of their action in this manner has yet been obtained.

* These figures were obtained with an apparatus similar in construction to the Rosenhain calorimeter.

CANDLES.

The materials chiefly used in the manufacture of candles are paraffin wax and stearic acid (which contains palmitic acid). Other substances used are beeswax, spermaceti and tallow.

Stearine candles, which contain a high percentage of stearic acid (not the glyceride stearin), are more suitable for use in hot climates than those containing much paraffin wax, on account of the fact that the melting-point of stearic acid is higher than that of most varieties of paraffin wax. Candles made of low melting-point paraffin wax are liable to bend and gutter.

Determination of the Melting-Point of Candle Waxes.

Fill a test tube, about one inch in diameter, to a depth of about two inches with the molten wax. Support the test tube vertically by means of a clamp.

Fix a thermometer in the test tube by means of a cork which has a vertical slit cut in its side. Adjust the height of the thermometer so that the bulb is mid-way between the surface of the wax and the bottom of the test tube.

Procure a stirrer made from a piece of wire bent at one end into a circle which just fits in the test tube, and then bent so that the circle fits round the thermometer. Make sure that the stem of this stirrer will move up and down freely through the slit in the cork.

Allow the molten wax to cool, and note the temperature indicated by the thermometer every half minute, keeping the molten wax gently stirred. Continue to take the readings until the material is completely solidified.

Plot the results in the form of a curve, with temperatures as ordinates and times as abscissæ.

The temperature indicated at which the curve changes direction is taken as the melting-point of the wax.

In the diagram, Fig. 34, the cooling curves are shown, (A) for a specimen of paraffin wax, and (B) for naphthalene.

The melting-point of the paraffin wax in this case is taken as 54° C. and of the naphthalene as 80° C.

Since naphthalene ($C_{10}H_8$) is a single compound and paraffin wax a mixture, the temperature of the former remains

constant during its complete solidification, but in the case of paraffin wax the temperature falls slightly during solidification. The reason for the temperature remaining constant, or nearly

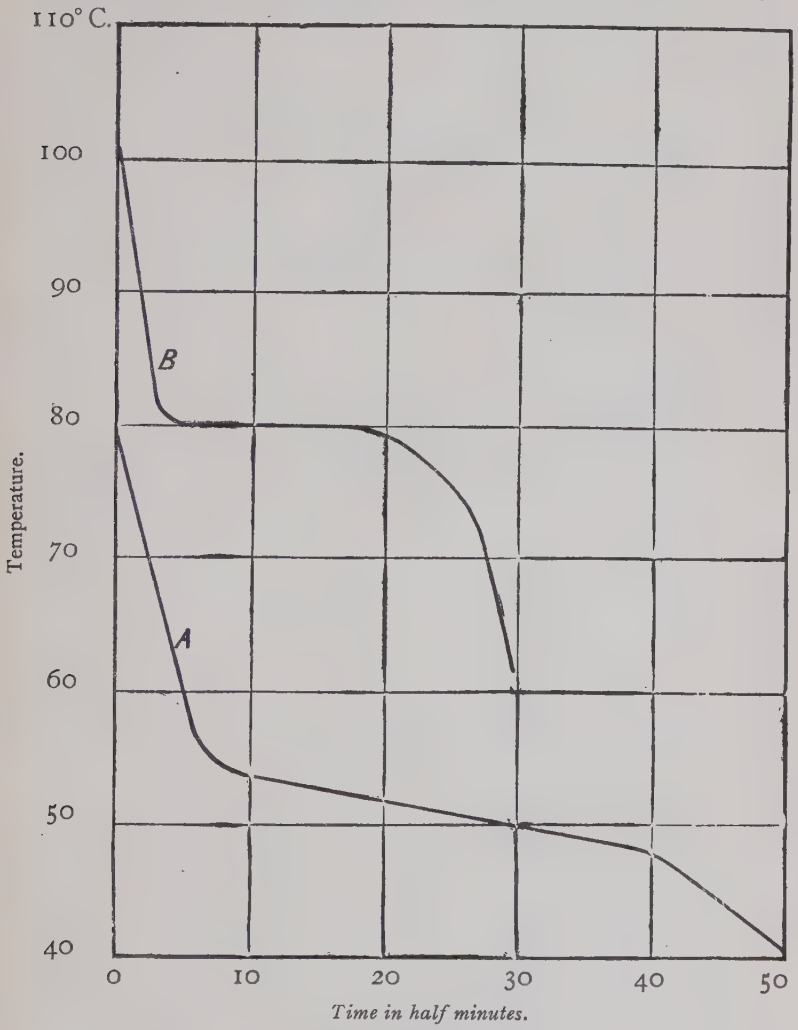


FIG. 34.—Cooling curves of (A) paraffin wax, (B) naphthalene.

so, during solidification is that during this process the latent heat of fusion of the substance supplies the heat which is lost by radiation, etc.

Determination of Stearic Acid in Candles.

The amount of free acid in a stearine, or composite, candle is determined by titration with a standard solution of an alkali, using phenolphthalein as indicator, since stearic acid is a weak acid.

Place 5 to 10 gms. of the material in a weighing bottle and weigh accurately. Transfer the substance to a flask and re-weigh the bottle, and so obtain the weight of substance taken for the test.

Add ether to dissolve the material; add about 10 c.c. of alcohol and a few drops of phenolphthalein solution. Warm the mixture on the water bath and titrate the solution with semi-normal sodium hydroxide solution, keeping the mixture warm.

From the equation

$$\underset{284}{C_{17}H_{35}COOH} + \underset{40}{NaOH} \rightarrow C_{17}H_{35}COONa + H_2O$$

it will be seen that 1 litre of normal sodium hydroxide solution (containing 40 gms. NaOH) will neutralise 284 gms. of stearic acid

or 1 c.c. N/2NaOH = 0·142 gm. $C_{17}H_{35}COOH$.

From the volume of sodium hydroxide solution required, the amount of acid, expressed as stearic acid, in the weight of material taken can be found, and from this the percentage of stearic acid calculated.

THE FUEL RATIONING ORDER, 1918.

FUEL ALLOWANCE.

By the terms of this order "fuel" may be taken as coal, gas or electricity, in accordance with the following scale—1 ton of coal is to be regarded as equivalent to 15,000 cub. ft. of coal gas, or 800 Board of Trade units of electricity.*

These values have been arrived at on the assumption that 1 ton of coal will produce approximately 15,000 cub. ft. of gas, or will generate sufficient power for the production of 800 Board of Trade electrical units.

The amounts of heat which could be generated by 1 ton of coal and these equivalents of gas and electricity are calculated as follows:—

* These figures refer to the Order of 1918, and have since been modified.

Coal.

Assuming the coal to have a calorific power of 8 Cal. per gram, i.e. 8000 Cal. per kg., 1 ton (1016 kg.) will produce
1016 × 8000 = 8,128,000 Cal. = 8,128,000 × 3·968
= 32,250,000 B.Th.U. (approx.).

Gas.

If the calorific power of the gas is taken as 120 Cal. per cub. ft.,

15,000 cub. ft. of gas will produce 120 × 15000 = 1,800,000 Cal. = 7,142,000 B.Th.U. (approx.).

Electricity.

From the relations

1 watt = 1 joule per second,
1 watt-hour = 3600 joules,
and 1 joule = 0·24 calorie,

1 watt-hour (or 3600 joules) = 3600 × 0·24 = 864 calories.
1 kilowatt-hour (Board of Trade electrical unit) = 864,000 calories = 864 Cal.

∴ 800 Board of Trade electrical units = 864 × 800
= 691,200 Cal. = 2,743,000 B.Th.U. (approx.).

Summary.—1 ton of coal would produce 8,120,000 Cal.
15,000 cub. ft. coal gas would produce 1,800,000 Cal.
800 Board of Trade electrical units would produce 691,200 Cal.

From these calculations it will be seen that by taking the fuel as coal, more than four times as much heat is theoretically obtainable than if the allowance is taken as gas, and about twelve times as much as if electricity is taken. Similarly nearly three times as much heat could be obtained theoretically from the 15,000 cub. ft. of gas as from the 800 units of electricity.

It must, however, be remembered that a greater efficiency is obtained in gas and electrical apparatus than is the case with coal (see pp. 229-231).

LIGHTING ALLOWANCE.

The amounts of coal gas and electricity allowed under the heading of lighting allowance are not in the same proportion as 15,000 cub. ft. of gas to 800 units of electricity (i.e. 16·8 cub. ft. of gas to 1 unit of electricity), but are in the proportion 15,000 cub. ft. of gas to 240 units of electricity (i.e. 62·5 cub. ft. of gas to 1 unit of electricity).

This basis is arrived at on the assumption that 1 Board of Trade unit of electricity and 62·5 cub. ft. of gas, used for purposes of illumination, produce lights of approximately equal intensity.

Thus if a 100 watt metal filament electric lamp and an incandescent gas burner, consuming 6·25 cub. ft. of gas per hour, give lights of approximately equal candle power * (about 90 c.p.), in one hour the electric lamp requires 100 watt-hours, or 0·1 unit, i.e. 1 unit in ten hours, and the gas burner will consume 6·25 × 10 = 62·5 cub. ft. of gas in ten hours.

FURTHER CALCULATIONS RELATING TO FUELS, ETC.

COAL GAS AS A SUBSTITUTE FOR PETROL.

Calculation of the volume of coal gas which is equivalent in calorific power to 1 gallon of petrol.

The coal gas is assumed to have a calorific power of 480 B.Th.U. (net) per cub. ft., and the petrol (density 0·7) 10·5 Cal. (net) per gm.

1 gallon of water = 10 lb. = 4536 gms.

1 „ petrol = 0·7 × 4536 = 3175·2 gms.

∴ Calorific power of 1 gallon of petrol = 3175 × 10·5 Cal.
= 33337·5 Cal.

Calorific power of the gas = 480 B.Th.U. = $\frac{480}{3{\cdot}968}$ = 121 Cal. per cub. ft.

121 Cal. obtained from 1 cub. ft. of gas.

∴ 33337·5 Cal. obtained from $\frac{33337{\cdot}5}{121}$ = 267 cub. ft.

Thus 267 cub. ft. of the gas are equivalent to 1 gallon of the petrol.

For gas at 4s. per 1000 cub. ft., the quantity of gas

* See p. 221.

equivalent to 1 gallon of petrol would thus cost rather more than 1s.

For further information on this subject see "Interim Report of the Gas Traction Committee (1918), H.M. Petroleum Executive" (H.M. Stationery Office) and "Applied Chemistry Reports," Vol. II., 1917, p. 43 (Society of Chemical Industry).

COMPARISON OF THE COST OF HEATING BY MEANS OF A GAS FIRE AND AN ELECTRIC RADIATOR (UNENCLOSED PATTERN).

Assuming that the consumption of gas per hour is 40 cub. ft. and the calorific power of the gas 120 Cal. (net) per cub. ft., the amount of heat generated per hour = 40 × 120 = 4800 Cal.

On the assumption that 25 per cent. of this heat is lost as flue heat, the amount of heat obtained as convected and radiant heat from the gas fire is $\frac{3}{4} \times 4800 = 3600$ Cal. per hour.

At 3s. 4d. per 1000 cub. ft., 40 cub. ft. of gas cost approximately 1·5 pence, or 3600 Cal. for effective heating are obtained for 1·5 pence.

An electric radiator required 12·5 amperes at 200 volts.;

i.e. 12·5 × 200 = 2500 watts* = 2·5 kilowatts, or in one hour 2·5 units.

From the relation

1 kilowatt hour = 864 Cal. (see p. 261),

$2\frac{1}{2}$ kilowatt hours = 864 × 2·5 = 2160 Cal.

At 2·5 pence per unit, 2·5 units cost 6·25 pence.

Thus with the electric radiator for 6·25 pence 2160 Cal. are obtained.

For 6·25 pence with the gas fire, the amount of effective heat $= \frac{3600 \times 6{\cdot}25}{1{\cdot}5} = 15{,}000$ Cal.,

that is, under the conditions given, nearly seven times as much heat for the same expenditure.

FIRE EXTINGUISHERS.

In order to extinguish a fire it is necessary to reduce the temperature, as for example by the use of water, or to exclude oxygen (by use of sand, a blanket or other woollen material) from the burning material. In some types of fire extinguisher

* Amperes × volts = watts.

these two aims are combined. Thus in many types of apparatus, when the extinguisher is required for use, a solution of hydrochloric acid is allowed to come in contact with a solution containing excess of sodium bicarbonate, the resulting stream of water highly charged with carbon dioxide is then directed on the base of the fire. The carbon dioxide and steam which are generated exclude the air from the burning material. The water reduces the temperature, partly owing to the heat required to remove it by evaporation, and partly by driving the flame from the surface of the burning material. A protective film of sodium chloride and carbonate, formed by decomposition of the excess of bicarbonate, is produced on the surface of the burning material.

In other forms of apparatus solutions of sodium chloride, ammonium chloride, calcium chloride, sodium sulphite, etc., are employed. Apart from the cooling effect of the water, incombustible gases are formed in some cases, and a layer of non-combustible substance is left on the burning surface.

Another type of fire extinguisher consists of a metal pump by means of which a stream of a non-inflammable, volatile, organic liquid, such as carbon tetrachloride, CCl_4, is directed on the fire. The vapour produced by the evaporation of this liquid excludes the air from the burning material. These appliances are useful in dealing with petrol burning in a confined space. The use of water in such cases would probably lead to an extension of the fire, as the burning oil will float on the surface of the water.

The use of carbon tetrachloride as a fire extinguisher may be illustrated by setting fire to a small quantity of light petroleum in a beaker, when it will be observed that by the addition of carbon tetrachloride to the burning material the flame is extinguished. The addition of water to the burning petrol will not extinguish the flame.

A solid mixture which consists of approximately 40 per cent. sodium bicarbonate and 60 per cent. calcium carbonate is also employed as a fire extinguisher. Such mixtures when applied to a fire will produce carbon dioxide, and form a protective layer on the surface of the burning material; their use, however, except for fires of a very limited extent does not appear to be reliable. The same applies to fire extinguishers of the grenade type.

The analysis of the materials used for the various types

of fire extinguishers may be carried out by the ordinary methods.

The relative merits of the various forms of apparatus and substances employed for extinguishing fires are discussed in articles in "Nature," 1915, pages 373 and 565.

COAL TAR DISINFECTANTS.

SOLIDS.

In the solid preparations crude carbolic and cresylic acids, containing phenol, C_6H_5OH, and o., m. and p. cresols, $C_6H_4(CH_3)OH$, together with some hydrocarbons, are mixed with an inorganic substance such as calcium carbonate, calcium sulphate, slaked lime, etc.

To determine the percentage of phenols in such a mixture, a weighed amount (about 50 gms.) is extracted with ether in a Soxhlet extraction apparatus (see Vol. II.). In this way the phenols and hydrocarbons are obtained in ethereal solution. If the original powder contains free alkaline hydroxide, such as calcium hydroxide, it is necessary to acidify with sulphuric acid (1 part of acid to 1 of water) before extraction with ether, care being taken that the temperature is kept low, otherwise phenols will be lost.

The ethereal solution is then treated in a separating funnel with two successive portions, of about 20 c.c., of 20 per cent. sodium hydroxide solution. The phenols are thus converted into phenoxides which are soluble in the water, and the hydrocarbons remain dissolved in the ether.

The combined sodium hydroxide extracts are then evaporated on a water bath to about 10 c.c., the solution being first heated by immersion in hot water, well away from any flame, until the ether retained has been expelled.

The solution of the phenoxides is then transferred to a small graduated cylinder and acidified with sulphuric acid (1 : 2). The volume of the phenols liberated is read off when the mixture is quite cold. On the assumption that 1 c.c. of the mixed phenols = 1·05 gm.,* the percentage by weight of phenols in the original powder may be calculated. This varies, as a rule, from 10 to 20 per cent. in such preparations.

In another method for determining the phenols, a weighed quantity of the powder, after acidification, is distilled in steam,

* Although the mixed phenols are specifically heavier than water they will float on the solution of sodium sulphate.

the phenols and hydrocarbons in the distillate being separated after extraction with ether as described above.

LIQUIDS.

These preparations usually consist of mixtures of a fraction of a coal tar distillate, rich in phenols, with soap and water. Resin is also sometimes used in their manufacture. In some cases the coal tar distillate is mixed with fat, which is then saponified.

Cresols are only slightly soluble in water, but when mixed with soap give liquids which remain clear on dilution with water.

The most important test in connection with these liquid disinfectants is that known as the Rideal-Walker test, in which the actual bactericidal property of the preparation is compared with that of a solution of phenol of known concentration.

The operations involved in one method for the purely chemical analysis of such mixtures, however, are as follows :—

Five to 10 gms. of the liquid in about 100 c.c. of warm water are treated with about 50 c.c. of 10 per cent. sodium hydroxide solution, whereby the phenols are completely converted into phenoxides, if not already present in this form. The hydrocarbons are then extracted by means of ether.

To determine the amount of these hydrocarbons, the ethereal solution is dried over anhydrous potassium carbonate and transferred to a dry, weighed flask. The ether is then distilled off (see p. 170), the flask and residue dried in a desiccator over sulphuric acid and weighed.

After the ether has been removed by immersing the flask in hot water, the alkaline solution containing the phenoxides, soap, etc., is neutralised by the addition of hydrochloric acid, the acid being added until a slight turbidity is produced.

About 15 gms. of solid barium hydroxide is then added to the solution, a reflux water condenser is attached, and the mixture heated on the water bath for about half an hour, with frequent shaking.

The barium salts of the acids present in the soaps, etc., which are insoluble in water, are then filtered off from the cold liquid through teased asbestos, by means of a water pump. The filtrate, which contains the phenols as barium phenoxides, is then acidified with hydrochloric acid and the phenols extracted by means of ether. The ether is evaporated off and the residue of mixed phenols weighed. (See also separation of phenols from soap, p. 69.)

Chapter X.

MATERIALS USED FOR THE PROTECTION OF WOOD, METAL AND OTHER SURFACES.

PAINTS.*

Oil Paints.

The three essential constituents of an oil paint are the medium, pigment and drier.

The *medium* usually consists of linseed oil,† which by absorption of oxygen, on exposure to air, is converted into a solid substance, and in this way the paint hardens. Polymerisation also takes place when the oil is exposed to air, with the production of solid substances.

The linseed oil, which is used in paint manufacture, is often previously heated to about 150° C. with a drier (see p. 269), as by this treatment the rate at which oxygen is subsequently absorbed by the oil is greatly increased. The oil which has been treated in this manner is known as "boiled oil".

The glycerides present in linseed oil are derived very largely from unsaturated acids, and the absorption of oxygen takes place at the double bonds. In the presence of certain salts of lead and manganese (driers) this absorption of oxygen is accelerated. These salts probably interact with the free acids formed by the partial decomposition of the glycerides of the oil, and the resulting compounds act as catalytic agents.

The gain in weight of linseed oil on exposure to air may be illustrated by spreading a thin layer of the substance‡ over the inside of a weighed petri dish, and noting the increase in the weight of the dish and oil at regular intervals.

* The subject of paints, varnishes, etc., is only dealt with very briefly; for further information books of reference must be consulted.

† During the war a large amount of paint has been made in which medium consists of the free acids obtained from linseed oil.

‡ Putty, which is a mixture of "boiled" linseed oil and whitening or whiting ($CaCO_3$), may also be employed for this purpose.

It will be noticed that absorption of oxygen produces at first an increase in volume, as shown by the production of furrows on the surface of the oil, but as oxidation proceeds contraction takes place, the final product of oxidation occupying a less volume than the original oil. This contraction leads to the formation of cracks in paint which has been applied to a surface for a long time.

Turpentine is often added to the oil to facilitate the distribution of the paint. This substance, unlike linseed oil, volatilises on exposure to air.

The *pigment* is usually a very finely powdered amorphous substance insoluble in the medium. In determining whether or not a substance is suitable for use as a pigment, it is necessary to consider (*a*) the permanence of the colour, or in the case of a white pigment its power of resisting discoloration by sulphuretted hydrogen, (*b*) its covering power and body, or opacity; that is, the extent to which it can be spread over a surface and at the same time completely conceal the surface below, (*c*) its drying power, that is, its action in promoting absorption of oxygen by the oil.

By far the most important substance used as a pigment is white lead or basic lead carbonate, $2PbCO_3 . Pb(OH)_2$. This substance has great covering power and opacity, and is used in the manufacture of a large number of paints, other pigments being added to give the necessary colour. Basic lead sulphate is sometimes used as a substitute for white lead.

Owing to the fact that lead is a cumulative poison, the use of white lead is open to serious objection from the point of view of those engaged in the manufacture and application of paint, and another objection to its use is that it is discoloured on exposure, owing to absorption of sulphuretted hydrogen. For these reasons a mixture of zinc sulphide and barium sulphate (lithopone) is largely used as a substitute for white lead.

For black paints lampblack is extensively employed.

For coloured paints both organic and inorganic compounds are used, the latter as a rule being more permanent.

Yellow paints may contain hydrated ferric oxide (yellow ochre), lead chromate (chrome yellow), cadmium sulphide, etc.

Calcined ferric oxide is used for brown paints.

Red paints contain red lead, mercuric sulphide, etc.

Prussian blue and indigo are used for blue paints and Prussian blue with lead chromate for green paints. Copper

and chromium compounds are also used for this purpose.

The *drier* is a substance usually added to a paint in order to accelerate the absorption of oxygen by the oil. Manganese borate, lead acetate, litharge, etc., are used for this purpose.

The Partial Analysis of an Oil Paint.

In carrying out an analysis of an oil paint, the volatile matter is first determined by heating 2 to 3 gms. of the paint in a weighed, flat bottomed porcelain basin for two hours in an air oven at 100° C. The dish is then weighed and the heating continued as long as the paint loses weight.

For the examination of the oil and pigment (and drier) the procedure is as follows :—

Ten to 15 gms. of the well-mixed paint are weighed into a beaker and 25 c.c. of light petroleum added, any lumps being broken up by means of a glass rod, 40 c.c. more of light petroleum are added, and when the pigment has settled to the bottom of the beaker, the clear liquid is poured off through a tared filter paper into a tared flask. The pigment is washed with successive small quantities of light petroleum and the washings poured through the filter. The pigment is finally transferred to the filter, dried in the steam oven and weighed on the filter paper.

The Oil.—The light petroleum is evaporated from the oil by heating on the water bath (see Fig. 10, p. 170). The flask and oil are then dried in the steam oven and weighed.

If the physical and chemical constants of the oil (specific gravity, refractive index, saponification and iodine values) are to be determined (see Vol. II.) the light petroleum should be removed by means of a stream of carbon dioxide, to prevent oxidation of the oil.

The Pigment (and drier).—If the original paint contained varnish, or other substance not extracted by light petroleum, the pigment obtained after removal of the oil will be sticky. In this case the resins mixed with the pigment may be extracted by means of alcohol, chloroform, carbon tetrachloride, etc., after the extraction with light petroleum.

If the paint contained an organic colouring matter, which is sometimes present in red and green paints, some of this will be removed by the alcohol, especially if the residue is previously acidified with hydrochloric acid (see "Colouring Matters in Foods," Vol. II.).

The pigment, free from oil and varnish, may now be analysed qualitatively and quantitatively by the usual methods.

VARNISHES.

These preparations consist of various resins dissolved in oil (usually "boiled" linseed, or tung oil), turpentine, alcohol, or sometimes aqueous solutions of alkalis. Coal tar naphtha and light petroleum are also employed in their manufacture.

In the preparation of oil varnishes, the hot oil is usually added to the fused resin, and in this way the properties of the oil are considerably modified.

The composition of the preparation varies according to the purpose for which it is employed. Thus with an oil varnish, which is suitable for surfaces exposed to the open air, the oil forms part of the dried covering and a durable varnish is obtained. Turpentine varnishes dry more rapidly owing to the evaporation of the solvent. Alcohol (spirit) varnishes dry very quickly, but the resin left behind is liable to scale off.

Enamel paints, or enamels, usually consist of oil varnishes to which a pigment in an *extremely* fine state of division has been added. For white enamels zinc oxide is usually employed, on account of its greater degree of fineness as compared with white lead.

The examination of varnishes is a matter of considerable complexity and will not be dealt with here. Evidence as to the nature of the solvent employed may, however, be obtained by distillation in steam.

The use of solutions of resins for lacquering, japanning and French polishing will be dealt with in the lectures.

WATER PAINTS, DISTEMPERS, WHITEWASH.

In these preparations the medium, water, contains various substances in suspension and solution.

In *whitewash* calcium carbonate, known as whitening or whiting, which has been washed by soaking in water, allowed to settle and strained through a fine sieve, is mixed with a solution of size.

A small quantity of ultramarine, or other blue colouring matter, is added to counteract the yellow colour of the whiting.

Distempers are usually emulsions containing water, calcium carbonate or sulphate, soap, glue, oil, resin and colouring

matter. Casein is also used in some cases, and small quantities of phenols are sometimes present in these preparations.

Water paints usually contain a larger percentage of oil, and in some cases calcium stearate is present.

The following series of tests may be applied to the above mixtures after the removal of water by drying :—

(*a*) Extraction of oil, together with any fat and fatty acid present, by means of ether.

(*b*) Extraction of soap, resin and possibly some colouring matter by means of alcohol. The soap should be tested for by evaporation of the alcohol, solution in water and separation of fatty acid (see p. 61).

(*c*) Extraction of glue by water and its precipitation from the aqueous solution so obtained by tannic acid or alcohol.

After extraction of the soap with alcohol, the residue should be acidified with hydrochloric acid, and the stearic acid, obtained from the calcium stearate, extracted by means of chloroform.

Phenols are tested for by distillation in steam, after acidification.

The inorganic colouring matter, which may be chromium oxide, an ochre, etc., will remain behind after extraction of the oil, soap, etc., and should be tested for in the usual way.

If an organic colouring matter is present, some of it will be extracted by alcohol, but in the case of a lake probably only after treatment with hydrochloric acid.

METAL POLISHES.

Liquids.

In general, liquid metal polishes consist of mineral matter suspended in a solution of an organic acid, such as oleic acid, in paraffin oil. In some cases, however, a mixture of alcohol and water is used instead of paraffin. The mineral matter as a rule consists of a very finely powdered aluminium silicate, but substances such as calcium carbonate, silica and rouge are also employed. Ammonia, sodium carbonate or soap are present in some of these preparations.

The mode of action of such polishes is partly of a mechanical, and partly of a chemical nature. Oxides and sulphides of metals, which are produced on the surface of metals when they tarnish in air, are usually readily soluble in acids, but it is essential that only such acid or other substance, as is without pronounced action on the metal itself, shall be used in a

metal polish. Thus mineral acids are quite unsuitable for use in these preparations. The object of the addition of paraffin oil, or alcohol, to these polishes is to facilitate the removal of grease from the surface of the metal. The mineral matter is added to help in the mechanical removal of the tarnish, and in the production, by polishing, of the necessary smooth thin film of metal on the surface polished. It will be obvious that this mineral matter must be free from large or gritty particles, otherwise the surface is scratched. It is very important in using these polishes that none of the mixture be allowed to remain on the surface of the metal, otherwise re-tarnishing takes place very quickly.

The analysis of liquid metal polishes usually consists of determinations of volatile matter, oleic acid, mineral matter and the flash point.

(*a*) *Volatile Matter and Residue.*—5 gms. of the well-mixed polish are heated in a porcelain basin on the water bath, until nearly all the volatile matter is expelled. The dish is then heated in the steam oven until the weight is constant.

If the residue is alkaline, it is treated with warm water and filtered. The filtrate is tested for sodium carbonate and soap (see p. 74).

In order to ascertain the nature of the volatile matter, 50 gms. of the polish are distilled in steam. The oil, which separates in the distillate, is removed by means of a separating funnel, dried over calcium chloride and distilled, the range of temperature over which distillation takes place being noted (see p. 169). This oil will usually be a mixture of paraffin hydrocarbons, in some cases, however, it may be a coal tar naphtha or turpentine.

(*b*) *Acidity.*—20 gms. of the polish (containing paraffin) are diluted with an equal volume of light petroleum and filtered into a flask. The extraction is repeated with successive small quantities of light petroleum, which is then evaporated from the combined extracts. The residue in the flask, consisting of oleic acid, heavy petroleum, etc., is heated on the water bath with 50 c.c. of alcohol (which is neutral to phenolphthalein) and the solution titrated with N/10 sodium hydroxide solution, using phenolphthalein as indicator. In this way the percentage of oleic acid in the polish is determined.

Mineral acids should not be present in these polishes; they may be tested for in the solution obtained by shaking some of the polish with water.

Oxalic acid may be present, and the presence of a small quantity of this substance is not objectionable.

(*c*) *Mineral Matter.*—The mixture remaining after extraction with light petroleum (*b*) may be extracted with alcohol for removal of soap, and with water for removal of sodium carbonate, etc. The residue may be examined for grit by rubbing some of it in a basin with a flat-headed glass rod.

(*d*) *Flash Point.*—This determination is of importance in connection with the storage of these preparations. It is carried out as described on page 247.

If alcohol is present in a liquid metal polish, its amount may be determined as in the case of an alcohol-soap mixture, page 249.

Ammonia, if present, may be determined by distillation into a measured volume of a standard solution of an acid. (See Kjeldahl Determination of Nitrogen, Vol. II.)

Polishing Pastes.

With these preparations the following series of tests may be carried out :—

(*a*) Determination of volatile matter.

(*b*) Extraction by ether for removal of fat, fatty acid and mineral oil. The fatty acid in the residue, obtained after removal of the ether from this extract, is determined as described on page 272. Another portion of the residue is boiled under reflux for half an hour with semi-normal alcoholic sodium hydroxide solution, whereby the free fatty acid is neutralised and any fat present saponified. Mineral oil, vaseline, or other unsaponifiable matter, remaining in the soap solution thus obtained, is extracted after dilution with water by means of light petroleum. The total residue from the ethereal extract, less the sum of the fatty acid (calculated as oleic acid) and the mineral oil, gives the amount of fat. (Compare unsaponifiable matter in soap, p. 68.)

(*c*) Extraction of the residue with alcohol for the removal of soap, after removal of the fat, fatty acid and mineral oil, followed by extraction with water for removal of sodium carbonate, etc. (see Chapter III.). The final residue is then tested for grit as described above.

(*d*) Testing for mineral acids in an aqueous extract of the original paste.

Nitrobenzene is usually added in small quantity to these preparations to mask the odour of the fatty acids.

The Use of Aluminium and Soda for Removing Tarnish.

Metals which are not attacked by solutions of alkaline carbonates, e.g. silver, may be cleaned by placing the tarnished surface in contact with a piece of aluminium foil, which is then immersed in a warm solution of sodium carbonate or washing soda.

The aluminium dissolves in the alkaline solution with the evolution of hydrogen; the oxides and sulphides of which the tarnish is composed are thus reduced, leaving a clean metallic surface.

The following equation shows the reaction between the aluminium and sodium carbonate:—

$$Na_2CO_3 + 2Al + 3H_2O = Na_2OAl_2O_3 + 3H_2 + CO_2.$$

Sheets of metal are now sold for this purpose under various names, and may be shown by the usual qualitative reactions to be composed of aluminium.

Powders sold for use with the metal should be examined in the manner described for water softeners (see p. 36).

FURNITURE POLISHES.

These preparations are usually mixtures of substances such as beeswax, paraffin wax and turpentine. Sometimes, in addition, they contain soap and water.

In analysing such a mixture the volatile matter would be determined and the residue extracted with ether for removal of wax. The relative proportions of beeswax and paraffin wax in a mixture of these two substances is determined as described in Vol. II. After extraction with ether, any soap in the residue may be extracted by means of alcohol.

BOOT POLISHES.

Black boot polishes often consist of mixtures of a saponifiable oil or a wax, such as beeswax, carnaüba or paraffin wax, with sugar, sulphuric acid, glycerine, turpentine and finely divided carbon, such as lampblack or animal charcoal.

By the action of sulphuric acid on animal charcoal the

carbon is set free in a very fine state of division, the calcium phosphate being converted to acid calcium phosphate, which leads to the removal of the sulphuric acid. Carbon is also set free from the sugar by the sulphuric acid.

This acid, if present in excess, would lead to the destruction of the leather to which the polish is applied.

Owing to the hygroscopic nature of glycerine, the presence of this substance in a boot polish serves to keep the latter moist. It also facilitates the distribution of the polish, keeps the leather soft and prevents the growth of moulds in the preparation.

In analysing these mixtures the volatile matter is first determined. Its nature is ascertained by steam distillation, as described under liquid metal polishes.

Oil and wax are extracted by means of ether from the dried material. Extraction with alcohol of the part insoluble in ether will remove glycerine, some sugar and possibly a dye. After evaporation of the alcohol, glycerine is tested for by means of the borax test (see p. 58).

Sugar may be determined in an aqueous extract of the preparation, by means of Fehling's solution, before and after inversion (see Vol. II.).

The amount of carbon is determined by noting the loss in weight on igniting some of the dried residue obtained after extraction with ether, alcohol, and water. If bone black was used in the preparation of the material, a residue containing calcium phosphate will be obtained after the removal of the carbon.

Free acid or alkali may be determined in an aqueous extract of the polish.

In brown polishes yellow ochre or other pigment is used instead of carbon.

GLAZES AND ENAMELS.

The methods employed for the production and glazing of pottery ware, china, etc., and also of enamels, will be considered in the course of the lectures. It is, therefore, only necessary here to discuss briefly the nature and properties of glazes and enamels, with reference to their use for various household utensils, and to describe the methods which may be employed for examining such articles in the laboratory.

GLAZES.

Pottery ware can be coated with a vitreous layer or glaze, which renders it impervious to liquid, and which may also be used for carrying out decorative designs.

Such glazes are composed essentially of an easily fusible glass, frequently a lead glass, and consist, after fusion, of silicates, or of silicates and borosilicates of alkali and alkaline earth metals and possibly of lead.

Other metallic oxides may be added with a view to producing (*a*) a coloured glaze for which purpose oxides of manganese, cobalt, etc., may be used, or (*b*) an opaque glaze or *enamel*, for which purpose stannic oxide (SnO_2) is usually employed. (See also Enamels, p. 282.)

The raw ingredients used for the production of glaze are chiefly: felspar, china clay, chalk, flint, sand, boric acid, borax, potash, soda and compounds of lead, e.g. litharge, red lead and white lead.*

The glaze is applied in the form of a fine suspension in water, and the soluble ingredients borax, soda, etc., are previously rendered insoluble by fusing with a portion of the ingredients containing lime, alumina, and silica, e.g. china clay, felspar, etc., whereby insoluble silicates and borosilicates are formed, and a glaze with better physical properties obtained.

The fused mass is run into water to separate it in a granular condition and in this form is known as "*frit*". In some cases the whole of the ingredients are "fritted," i.e. subjected to preliminary fusion before being used.

The ingredients of the glaze should be adjusted so that the coefficient of expansion of the glaze is as nearly as possible equal to that of the underlying body, or cracking and separation of the glaze from the material will occur.

Lead in Glaze.

In china and earthenware glazes the lead calculated as lead monoxide (PbO) may be from 10-20 per cent., occasionally more, and averages about 17 per cent.

* *Felspar*, a name given to certain naturally occurring silicates of sodium, potassium and aluminium, sometimes containing lime (lime-felspar). *China clay or kaolin*, $Al_2O_3 . 2SiO_2 . 2H_2O$, produced by the weathering of felspar. *Flint and sand*, SiO_2. *Litharge*, PbO. *Red lead*, Pb_3O_4. *White lead*, basic carbonate of lead, $2PbCO_3 . Pb(OH)_2$.

In a good "*insoluble*" glaze, however, the proportion of "*soluble lead*," i.e. lead which is soluble in dilute acids, should be very small.

Method of Determining Soluble Lead in a "Frit" or Glaze.—The British official method is as follows :—

One gram of the dried glaze or frit, ground ready for use, is shaken continuously for an hour with 1000 times its weight of a 0·25 per cent. solution of hydrochloric acid. After being allowed to settle for an hour, an aliquot portion is filtered off, the silica separated by evaporation in the usual way, the lead precipitated as sulphide, and finally weighed as sulphate.

In this country potters who use no glaze yielding more than 5 per cent. of "soluble lead," as thus determined, are exempted from certain restrictions. Further exemptions are allowed where the glaze used gives not more than 2 per cent. of soluble lead.*

Lead Dissolved from Finished Ware.—Unless the lead is completely converted into insoluble compounds on fusion, the more soluble portions will be extracted by the action of dilute acids on the glaze of the finished article, e.g. by the action of vinegar or fruit acids such as may be used for culinary purposes.

In Germany the manufacture and sale of glazed ware for culinary or drinking vessels, which yields any soluble lead compound on boiling with 4 per cent.† acetic acid for half an hour is prohibited, but in this country there is no standard test other than that mentioned above.

Examination of Glazed Pottery Ware.

The complete chemical analysis of a glaze can be carried out by methods similar to those used for the analysis of glass. The processes involved are complex and need not be dealt with here, but glazed articles such as are used for ordinary household purposes may be conveniently examined in the manner indicated below.

Flaws in the Glaze.—A good glaze should present a smooth, uniform surface. If a finely divided coloured powder

* Lead in an insoluble form is less injurious than soluble lead to the workers who apply the glaze, and Oliver ("Dangerous Trades," Murray) advocates the adoption of the 2 per cent. standard of solubility and suggests that all lead glazes should be fritted before use.

† A good vinegar may contain 5 per cent. of acetic acid, see Vol. II.

is rubbed over the surface, it will collect in any small cracks or pits in the glaze, and these will show up when the surface is examined with a magnifying lens.

Graphite may be used for light-coloured glazes and powdered talc for dark-coloured glazes.

Stability of the Glaze towards Weathering.—The stability of a glaze towards prolonged exposure to atmospheric conditions is usually tested by exposing the glaze to the action of hydrochloric acid gas for twenty-four to thirty hours.

The experiment may be carried out in a bell jar which fits air-tight on to a glass plate. A shallow porcelain dish containing concentrated hydrochloric acid is placed on the glass plate. Two narrow porcelain or glass strips are placed across the rim of the dish and on these the article to be tested is supported. The article is so placed that the glaze is directly exposed to the acid fumes, and the whole is then covered with the bell jar and allowed to stand for twenty-four to thirty hours.

The appearance of the glaze is observed and any white deposit formed is washed off and examined qualitatively.

Soluble Lead in the Glaze.—The examination of the glaze for soluble lead is most important in the case of vessels used for culinary purposes, e.g. casseroles,* etc. Such vessels when boiled with solutions of organic acids, e.g. acetic, malic and citric acid, such as might be used in ordinary processes, frequently yield appreciable quantities of lead. (See Masters, "The Analyst," 1919, **44**, 164.)

The amount of lead extracted will of course depend on the extent of glazed surface exposed to the action of the acid, and in order to obtain a fair comparison in testing vessels of various sizes and shapes the results are usually expressed as *milligrams of lead mononide* (PbO) *extracted per square decimetre of the glaze.*

Since it is difficult to calculate with any degree of accuracy the area of the surface attacked, if the glaze is only partially covered by the acid, it is advisable to fill the vessel nearly full with the acid solution, allowing just sufficient margin for boiling.

* *Casseroles*, the vessels here referred to, are those made of brown pottery ware and glazed on the inside; vessels made of "fire-proof china" or porcelain, which have a glazed surface both inside and out, do not as a rule yield any soluble lead, but articles made of ordinary "kitchen china," e.g. basins, pie-dishes, etc., sometimes yield small amounts.

** *To Determine the Soluble Lead in the Glaze of a Casserole.* —Find the capacity of the casserole by filling it with water from a graduated cylinder.

Measure into the casserole a volume of 4 per cent. acetic acid nearly sufficient to fill it, i.e. if the capacity is about 230 c.c. measure in 200 c.c. Place the casserole on a thin asbestos pad and heat over a flame.

Note the time when the liquid begins to boil, and continue to boil for half an hour. The vessel may be kept covered with the lid during this operation, and in this way any considerable diminution in volume during boiling is avoided.

Filter the solution if it is not absolutely clear. Rinse the casserole twice with a little hot distilled water and add these washings, after filtering if necessary, to the rest of the solution. When cold, make up the acid solution to its original volume or to any convenient measured volume, e.g. 250 c.c., etc.

Transfer 50 c.c. of the solution to a Nessler cylinder and add 2 c.c. of a saturated solution of sulphuretted hydrogen, stir with a clean glass rod and observe if any brown coloration is produced. The colour, if any, may vary from the least possible trace to a deep brown colour with incipient precipitation, and the procedure needs to be slightly modified according to the depth of colour obtained.

(1) If a distinct, but not very dark, brown colour is produced, it is first advisable to make sure that the coloration is due to the presence of lead and not to other metals (see p. 31). If the coloration is due to lead, the amount of this substance present in another 50 c.c. portion of the solution may be determined by matching the colour produced, on the addition of sulphuretted hydrogen, with that produced by a standard lead solution, in the manner described for the determination of lead in water (see p. 29).

From this the amount of lead present in the total volume of the acid solution, i.e. the total amount extracted from the casserole, can be obtained.

(2) If no colour or only a very faint coloration is obtained, transfer the remainder of the solution * to a porcelain dish, evaporate down to about 50 c.c. on a water bath, add a few drops of acetic acid and then again examine for lead, and determine the amount, if any, in the manner described above.

* If only a small volume of acid, i.e. 100 c.c., was used for the experiment there is no advantage to be gained by further concentration, and the lead found should be returned as a trace, or as nil, as the case may be.

In order to obtain the total lead extracted, allowance must be made in this case for the 50 c.c. of solution withdrawn for the first experiment, thus if the acid solution was made up to 250 c.c. and 50 c.c. withdrawn for the first experiment the lead found in the remainder of the solution should be multiplied by $\frac{250}{200} = \frac{5}{4}$ to give the total lead.

(3) If a very dark brown coloration is obtained, it is difficult to match the colour with any degree of accuracy, and the solution should be diluted before the matching is attempted.

Fifty c.c. of the solution may be diluted to 100 c.c. and 50 c.c. of the diluted solution used for the experiment. If the colour is still found to be too dark, the solution may be still further diluted.

Calculation of the Surface.—The area of the glazed surface can usually be calculated with sufficient accuracy from the dimensions of the vessel.

Thus casseroles are frequently nearly cylindrical in shape and in this case the surface is given by—

$$\begin{array}{ccc} \text{area of base} & + & \text{area of curved surface} \\ (\pi r^2) & + & 2\pi rh \end{array}$$

where r = radius of the base and h = height of the vessel.

Results of Examination for Soluble Lead in the Glaze of Casseroles.—As the presence of soluble lead in the glaze of casseroles is a matter of considerable practical importance, the results obtained with two different specimens are given in detail below.

Casserole, I.

Capacity of vessel = 140 c.c.

Diameter of base = 6·5 cm.
" " top = 6·0 " } *Mean* = 6·25 cm.

Depth = 5·5 cm.

Surface = area of base + area of curved surface
$= \pi \times (3{\cdot}3)^2 + 2\pi \times 3{\cdot}1 \times 5{\cdot}5$ sq. *cm.*
= 1·4 sq. *dm.*

One hundred c.c. of 4 per cent. acetic acid were boiled gently in the vessel for thirty minutes, and at the end of this time the solution was made up to the original volume.* 50 c.c.

*An approximately 4 per cent. solution of acetic acid is obtained by diluting 50 c.c. of commercial glacial acetic acid to 1 litre.

of the solution, on addition of sulphuretted hydrogen, gave a colour which was too dark to match. This colour was found to be due to lead.

The remaining 50 c.c. of the solution were diluted to 100 c.c. and 25 c.c. of the diluted solution were transferred to a Nessler cylinder and diluted to 50 c.c. On the addition of 2 c.c. of sulphuretted hydrogen solution, the colour obtained was matched by 3·5 c.c. of a standard lead solution, containing 0·1 mg. of lead per c.c. (see p. 30).

Thus 25 c.c. of the diluted solution contain 0·35 mg. of Pb.
And 100 „ „ „ „ „ 1·40 „ „
Or 50 „ „ original „ „ 1·4 „ „
And 100 „ „ „ „ „ 2·8 „ „
Hence the total lead extracted from the glaze = 2·8 mg.

And the *lead per sq. dm. of glaze* $= \frac{2 \cdot 8}{1 \cdot 4} = 2 \cdot 0$ mg.

Soluble lead is usually expressed in terms of the oxide PbO, and since

$$\frac{PbO}{Pb} = \frac{223}{207}, \text{ this gives } 2 \cdot 0 \times \frac{223}{207}$$

= 2·1 mg. of lead monoxide per sq. dm. of the glaze.

This experiment was repeated several times with the same vessel and lead was extracted in each case. The amount obtained in the second experiment was less than that in the first (viz. 1·7 mg. per sq. dm.), but did not afterwards diminish appreciably with successive treatments.

Casserole, II.

Capacity = 220 c.c. Diameter = 9·0 cm.
Depth = 5·0 cm.
Surface $= \pi \times (4 \cdot 5)^2 + 2\pi \times 4 \cdot 5 \times 5$ sq. cm.
= 1·7 sq. dm.

Two hundred c.c. of 4 per cent. acetic acid were boiled gently in the vessel for thirty minutes, and at the end of this time the volume of acid was made up to 250 c.c. 50 c.c. of this solution gave a faint brown tinge on the addition of sulphuretted hydrogen. The remainder of the solution (200 c.c.) was evaporated down to 50 c.c., and the colour then obtained on the addition of sulphuretted hydrogen was matched by 2 c.c. of the standard lead solution.

Hence 200 c.c. of original solution contain 0·2 mg. of Pb, or 250 c.c. contain $0{\cdot}2 \times \frac{5}{4} = 0{\cdot}23$ mg. of Pb.

Total lead extracted = 0·23 mg.

Lead per sq. dm. of glaze = $\frac{0{\cdot}23}{1{\cdot}7} = 0{\cdot}14$ mg.

Lead monoxide per sq. dm. of glaze = $0{\cdot}14 \times \frac{223}{207}$

= 0·16 mg.

ENAMELS.

Enamels are essentially glazes, which have been rendered opaque by the suspension of solid particles in the vitreous mass of which the glaze is composed. For this purpose, as already stated (see p. 276), stannic oxide (SnO_2) is chiefly employed, but other substances, e.g. antimony oxide * (Sb_2O_3) and calcium phosphate, are sometimes used.

Enamel may be used for coating earthenware, or may be applied to a metallic surface, e.g. iron, but the term *enamelling* is now often restricted to this latter process only.

The fusion of the enamel on to the metal must be carried out at a temperature below that at which the metal begins to soften, and the coefficient of expansion of the enamel must be as nearly as possible equal to that of the metal.

The enamelled articles used for household purposes are made from cast or sheet iron.

The basis of the enamel is generally a borosilicate glass which is often lead free.

** Examination of Enamelled Ironware.

Enamelled basins, saucepans, etc., may be examined in the following manner:—

Action of Dilute Acid on the Enamel.—Boil 4 per cent. acetic acid in the vessel for half an hour, as described for glazed pottery ware.

Concentrate the acid to a small volume (100 c.c.), divide into two portions, examine (*a*) for the presence of lead and iron, (*b*) for the presence of any dissolved solid matter.

*On account of its poisonous properties the use of antimony oxide is prohibited in Germany.

(*a*) Transfer the solution to a Nessler cylinder and make it just alkaline by the addition of colourless ammonium sulphide. Then proceed as described on page 31.

(*b*) Evaporate the solution to dryness and see if any appreciable residue is obtained.

Appearance of the Enamel.—The enamel if appreciably attacked by the acid will lose its gloss, and its appearance before and after the experiment should be carefully noted.

Examination of the Enamel for Lead.—In dealing with enamels and glazes which may contain lead, it is important to remember that only a small portion, if any, of the lead used is likely to be soluble in dilute acids (see p. 276) and that the tests already described deal only with the detection and determination of this *soluble* lead.

To detect the presence of lead in an enamel the following tests may be used :—

1. Moisten a small piece of filter paper with hydrofluoric acid, place upon the enamel and allow it to remain there for some minutes.

Wash off the paper, together with any pasty mass, into a platinium dish or crucible. Dilute with water and test for lead by the addition of sulphuretted hydrogen.

2. Moisten a small area of the enamelled surface with concentrated nitric acid. Heat until the acid has evaporated, moisten with a few drops of water followed by a few drops of a 10 per cent. solution of potassium iodide. The presence of even a trace of lead is sufficient to develop the characteristic yellow colour of lead iodide.

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